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In two volumes

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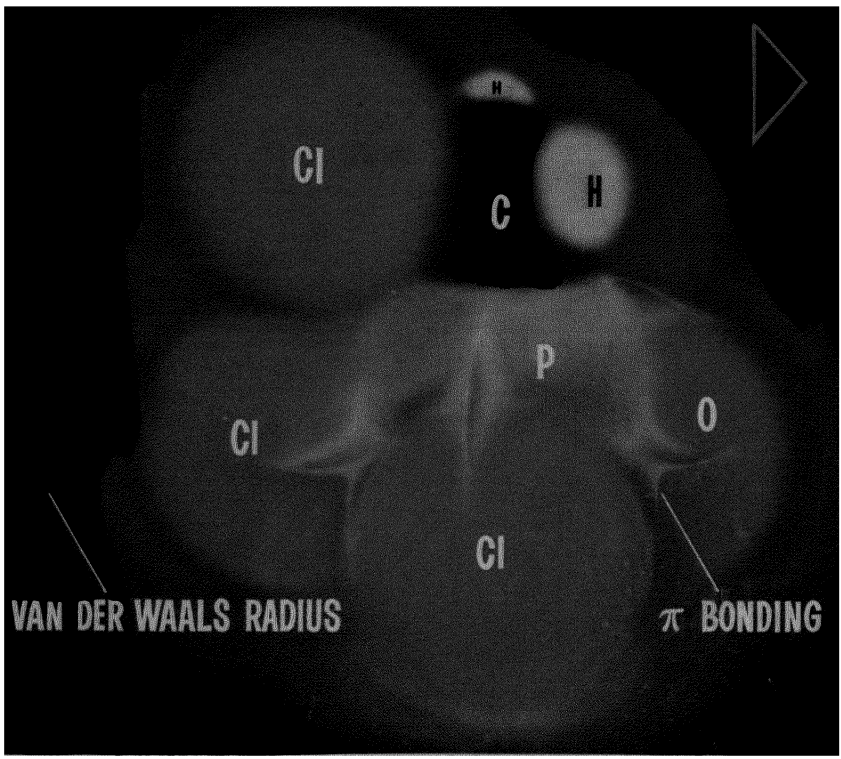

The compound $ClCH_2P(O)Cl_2$ showing π-bonding between the gray phosphorus atom and the two green chlorine atoms and single red oxygen atom attached to it. The van der Waals' radii of the atoms are denoted by the cloud surrounding the molecular structure.

PHOSPHORUS AND ITS COMPOUNDS

In Two Volumes

Volume I: CHEMISTRY

JOHN R. VAN WAZER

Assistant Research Director and Senior Scientist, Inorganic Chemicals Division, Monsanto Chemical Company, St. Louis, Missouri

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Dedicated to

BETTY and BETH

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PREFACE

The purpose of this book is to lay a foundation for a new, separate discipline of chemistry—phosphorus chemistry. Up to now, descriptive chemistry has been divided into two parts: organic chemistry, which treats of carbon compounds; and inorganic chemistry, which covers all that is left over. As now presented to the undergraduate student, organic chemistry is a beautifully systematic and self-consistent discipline, whereas inorganic chemistry has been somewhat of a hodge-podge of unrelated facts and often misguided fancy. Because of this, inorganic chemistry offers a tremendous challenge—a challenge which is being accepted by a sufficient number of persons today so that inorganic chemistry is undergoing a powerful renaissance. Three factors have made this renaissance possible. One of these—and perhaps the most important one—is the new qualitative and quantitative understanding of the interaction between atoms brought about by quantum mechanics in its two applicable forms—valence-bond and molecular-orbital theory. Another is the armament of powerful, new, structure-sensitive tools which have become generally available during the last decade or two for studying inorganic systems. The use of chromatographic methods, nuclear magnetic resonance, the techniques of polymer physics, as well as the older methods of x-ray and electron diffraction and vibrational analysis (infrared and Raman) point up the manyfold deficiencies of relying completely on wet-chemical analytical procedures for information, as has been done during most of the century and a half that inorganic chemistry has been a major chemical discipline. The third factor which has led to the inorganic renaissance is the ever-widening commercial interest in production of inorganic chemicals due in part to the fact that automation (the spirit of our Age) is so adaptable to inorganic processes which are run at large volumes.

But enough of inorganic chemistry, for this book treats of a different subject—phosphorus chemistry. Just as the organic chemist may develop the theme of, say, organic compounds of sulfur or of phosphorus—so I

have discussed the phosphorus compounds containing carbon from the viewpoint of a phosphorus chemist. In this book, no differentiation is made between the "inorganic" and the "organic chemistry" of phosphorus, except for the fact that the available data were obtained by persons having quite divergent philosophical viewpoints so that synthesis techniques, regardless of yield, are necessarily emphasized for the phosphorus compounds of carbon as opposed to phase relationships, crystal chemistry, and the like for the phosphorus compounds of other elements.

In setting up a philosophy for the nascent discipline of phosphorus chemistry, I have tried to take the best from both inorganic and organic chemistry. However, the spirit of the inorganic renaissance pervades this book, probably because a new discipline cannot afford the lordly but sketchy approach essayed by the organic chemist from the ramparts of his detailed chemical system.

And now you ask, why speak of a new discipline? Is it not sufficient to formalize the chemistry of phosphorus compounds within the confines of organic and the now rapidly developing inorganic chemistry? What a needless conceit to attempt the establishment of a new discipline

And I answer that there is a real need for a separate discipline just as there was a need for separating the chemistry of carbon compounds from the rest of chemistry Instead of being merely a ragtag collection, the compounds of carbon are readily arranged into homologous series, and a small number of ground rules have proved sufficient to describe the relationships and interactions between these homologous series and between members of a given series. This state of affairs also seems to apply to the compounds of phosphorus The phosphates, the phosphonitrilic chlorides, and other groups of phosphorus compounds are truly homologous series. Furthermore, a system of ground rules, in some cases quite different from those of organic chemistry, appears to be emerging Is this not a good reason for approaching the compounds of phosphorus with a fresh viewpoint and as a special topic?

In addition to its homologous series and rules, organic chemistry is also unique in that molecular structures can be built from "plans," by a process which I call "positional synthesis." Very little is said in this book about positional synthesis in phosphorus chemistry because very little has been done along these lines. However, there seems to be ample reason to believe that methods of positional synthesis can be developed specifically for phosphorus chemistry. This is an important challenge for the future.

Although the renaissance in inorganic chemistry is so new that it is difficult to predict its outcome, a broad pattern does seem to be emerging

According to this pattern, separate chemistries will probably be developed for those elements lying near carbon in the Periodic Table. This book represents an attempt in this direction for one such element—phosphorus

Throughout this book an effort has consistently been made to present available data in a form which will be useful to workers in the various areas of phosphorus chemistry. This means that, in some cases, extrapolations were employed and certain data were reworked and extended on the basis of the theories presented herein. In these cases, the text clearly states that the experimental findings were enlarged upon There are also occasional places where the data obtained by a certain author are used to prove a point which is in complete opposition to the original author's ideas. In cases where these original ideas are still believed by some people, a comment is usually made in the text that the interpretation given herein differs from the original. However, where the earlier interpretations are quite universally accepted as being obsolete, no mention is made of the reinterpretation.

No attempt has been made to review exhaustively the literature on phosphorus and its compounds. Indeed, it would take a book several times the size of this one to survey completely the literature on either the organic or the inorganic compounds of phosphorus. However, it is hoped that all of the classes of compounds (either organic or inorganic) which have received a reasonable amount of study are covered herein and that sufficient literature references are presented to enable the scholar to locate easily the entire literature on any particular subject of interest.

I wish to thank Julia D. Behrens for carrying out the extensive clerical work involved in preparing the manuscript of this book Thanks is also due to Celeste Frank for preparing the index and proofreading. In addition, I wish to acknowledge the technical assistance of John R. Parks in writing Chapter 12 and of Edmund Churchill of Antioch College in carrying out the mathematical calculations given therein. A review of phosphides prepared by Richard G. Yalman of Antioch College has also been of value in writing Chapter 4. In addition, I also gratefully acknowledge the corrections made on the page proof by John H. Payne, Donald P. Ames, Clayton F. Callis, John W. Cross, Allan D. Gott, Edward J. Griffith, Thomas L. Hurst, Chung Yu Shen, and Fritts W. Thomas, of Monsanto. Walter H. MacIntire, formerly of the University of Tennessee, John W. Gryder of Johns Hopkins University, and Oscar T. Quimby of Procter and Gamble have also assisted materially in improving the quality of this book. The continued encouragement and moral support of John L. Christian, Vice-President of Monsanto, have been greatly appreciated. Without his backing, this book could not have been written.

JOHN R. VAN WAZER

St. Louis, Missouri
May, 1958

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CHAPTER 1

The Phosphorus Atom, Its Nucleus and Electronic Structure

ATOMIC WEIGHT

Phosphorus, with an atomic number of 15, has six reported isotopes. Elements with odd atomic numbers exhibit no more than two stable isotopes; for phosphorus, there is one,[1] $_{15}P^{31}$. In accord with the laws of nuclear stability (modified Harkins' rules[2]), this stable isotope has an odd mass number, 31, to correspond with its odd nuclear charge, 15. The mass number of 31 is the closest whole number to the physical atomic weight of 30.9840 computed from nuclear reaction data and supplemented by mass spectrograph measurements.[3] This physical atomic weight is referred to the mass of the $_8O^{16}$ isotope taken as 16.000000. On the other hand, chemical atomic weights—universally used in chemical calculations—are based on the average mass of the naturally occurring mixture of $_8O^{16}$, $_8O^{17}$, and $_8O^{18}$ being equated to 16.00000. Although the naturally occurring mixture of oxygen isotopes has been shown to vary somewhat from source to source, the chemical atomic weight can be calculated from the physical one by dividing the latter by 1.00028—a factor based on an average relative abundance of the three oxygen isotopes. The presently accepted [1952] chemical atomic weight[4] of 30.975 for the single naturally occurring isotope of phosphorus was calculated by dividing the physical atomic weight by this factor. Chemical methods have not been used to evaluate the atomic weight of phosphorus since 1939, when a value of 30.98 was accepted,[4] primarily

[1] L. Kerwin, *Can. J. Phys.*, **32**, 757 (1954)

[2] T. Moeller, *Inorganic Chemistry*, John Wiley & Sons, New York, 1952, pp. 25–9.

[3] H. T. Motz, *Phys. Rev*, **85**, 501 (1952) [nuclear reaction data: 30.9840], H Ewald, *Z. Naturforsch.*, **6a**, 293 (1951) [mass spectrograph: 30.93622 ± 0.00023], C. D. Hodgman, *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., Cleveland, Ohio, 33d ed., 1951, gives 30.98441.

[4] E. Wichers, *J. Am Chem. Soc.*, **74**, 2447 (1952), also see A. F. Scott and M. Bettman, *Chem. Revs*, **50**, 363 (1952)

on the basis of the $POCl_3$:Ag ratio. The $POBr_3$:Ag ratio and the limiting density of phosphine vapor have also been used in atomic weight determinations of phosphorus.

NUCLEAR STRUCTURE[5]

Present-day concepts of nuclear structure indicate that the nucleus of an atom can be considered as being built up of neutrons and protons which are held together by transformations of one into another, such transformations being referred to as resonance or exchange processes Since the neutron is an elementary particle of unit mass and has no charge, whereas the proton has both unit mass and unit positive charge, the neutron-proton transformation can be formally represented as the transfer of a positive charge. This transfer, however, is a complicated process, believed to involve several mesons and the neutrino. According to this picture of nuclear structure, the stable isotope of phosphorus, $_{15}P^{31}$, has 15 protons and 31 − 15 = 16 neutrons at any instant. By subtracting the physical atomic weight of $_{15}P^{31}$ from the sum of the weights of 15 protons and 16 neutrons, the quantity of mass which disappears by transformation into energy can be calculated. From the Einstein equation, $E = mc^2$, this mass can be converted into energy terms. Thus, the binding energy of the stable phosphorus nucleus can be shown to be 8.4 M.e.v , or its equivalent of 2×10^8 kcal./gram-atom. Except for the lightest elements which have low nuclear binding energies (*e.g.*, 1.1 M.e.v. for $_1H^2$), binding energies per nucleon range from 7 through 8.7 M.e.v., with the maximum being reached at a mass number of 55 (iron). It should be noted that the packing fraction, mass defect, and other related quantities are relative measurements of the nuclear binding energy, which gives a direct measure of the energy released by taking the proper number of protons and neutrons (spaced infinitely far apart) and combining them into the nucleus in question. Since for phosphorus the number of either neutrons or protons lies between the magic numbers 8 and 20, there appear to be four closed shells in the nuclei of the phosphorus isotopes, with one unpaired proton in the fifth shell (2 *s*) accounting for the spin.

Nuclear Moments

Because of its odd mass number (sum of protons plus neutrons = 31), the mechanical or spin moment of the stable phosphorus nucleus must be an odd half-integer Analysis[6] of the alternating intensities of the rota-

[5] For example, see P F A Klinkenberg, *Rev Mod. Phys* , **24**, 63 (1952); M Goeppert Mayer, *Phys Rev* **78**, 16(1950); and R Serber, *Phys Rev* , **75**, 1459 (1949)

[6] M F Ashley, *Phys. Rev* , **44**, 919 (1933)

tional lines in the emission spectrum of diatomic phosphorus vapor has demonstrated that the nuclear spin of $_{15}P^{31}$ is $^1/_2(h/2\pi)$. This means that the electric quadrupole moment must be zero. The magnetic dipole moment, μ, of this nucleus has been shown to equal +1.1317 nuclear magnetons from measurement of the nuclear magnetic resonance of phosphoric acid, confirmed by a study of the spark spectrum of phosphorus vapor.[7] This value lies right in the middle of the theoretical limits for μ set by Schmidt.[8]

Elements which have a highly predominant isotope with a nuclear spin of $^1/_2$ and, hence, no quadrupole moment are the best suited for interpretation of the electronic structure of their molecules or molecule-ions from

TABLE 1-1[9]
Relative Abundance[a] in the Universe of Second-Row Elements

Atomic number	Element	Mass number	Isotopes with odd mass numbers	Isotopes with even mass numbers	All isotopes
10	Ne	20		42,000±	9,000–240,000
		21	130±		
		22		1,300±	
11	Na	23	462 ± 36		462 ± 36
12	Mg	24		6,970 ± 240	8,870 ± 250
		25	897 ± 97		
		26		1,000 ± 100	
13	Al	27	882 ± 81		882 ± 81
14	Si	28		9,228 ± 3	10,000
		29	467 ± 1		
		30		305 ± 3	
15	P	31	130		130
16	S	32		3,300	3,500
		33	26		
		34		150	
		36		0 56	
17	Cl	35	130		170
		37	42		
18	A	36		450±	130–2,200
		38		87±	
		40		?	

[a] Based on total silicon being set equal to 10,000.

[7] W. H Chambers and D Williams, *Phys. Rev.*, **76**, 638 (1949) [magnetic resonance]; and M. F. Crawford and J Levinson, *Can J Research*, **A27**, 156 (1949) [spectrum].

[8] T. Schmidt, *Z Physik*, **106**, 358 (1937)

[9] H Brown, *Revs Mod Phys.*, **21**, 625 (1949)

nuclear magnetic resonance data. Of the readily available elements exhibiting a reasonably complicated chemistry, only phosphorus, fluorine, and hydrogen fulfill these requirements. In a 10 kilogauss field, these three elements ($_{15}P^{31}$, $_{9}F^{19}$, and $_{1}H^{1}$) resonate at 17.24, 40.07, and 42.57 megacycles, respectively. At a constant magnetic field, their relative sensitivities for equal numbers of nuclei are 0.0664, 0.834, and 1.000, respectively. The use of nuclear magnetic resonance in structure analysis of molecules and molecule-ions is discussed in some detail on page 43.

Abundance of Nucleons

According to the Harkins' rules, the abundance of stable nuclei with odd mass numbers is considerably less than that of nuclei with even mass numbers. As shown in Table 1-1, phosphorus is the least abundant[9] of the elements in the second row of the periodic table, with chlorine and aluminum (which also have only isotopes with odd mass numbers) being the next least abundant. It is believed that the relative abundance of the elements is related to the origin of the universe; and several theories involving thermal transmutations in an extremely hot concentrated prestellar body, which later expanded to form the star-filled universe, have been worked out to explain the observed abundances and other data related to the existence of nuclei.[10]

Radioactive Isotopes

Data on the five radioactive isotopes of phosphorus are presented in Table 1-2.[11] The best known of these isotopes is $_{15}P^{32}$, which is made on a commercial scale in Oak Ridge by the S-*n*-*p* or P-*n*-γ reactions. The material from the S-*n*-*p* process can be obtained in an isotopically pure form. The manufacture[12] of the purified $_{15}P^{32}$ is carried out by irradiating about 2 kg. of specially purified sulfur in a large aluminum can in the atomic pile for about 6 weeks. This irradiation results in about 800 millicuries of $_{15}P^{32}$ and 350 millicuries of $_{16}S^{35}$ (half-life of 87 days) and some short-lived activities which decay to insignificance before the sample is shipped. The irradiated sulfur is melted out of the can, and the radioactive phosphorus, along with a small amount of the sulfur, is extracted with 0.2 *N* nitric acid

[10] R. A. Alpher and R. C. Herman, *Revs Mod Phys*, **22**, 153 (1950), for an elementary presentation, see G. Gamow, *The Creation of the Universe*, Viking Press, New York, 1952, pp. 44–73.

[11] J. M. Hollander, I. Perlman, and G. T. Seaborg, *Revs Mod Phys.*, **25**, 469 (1953)

[12] J. N. Butler and W. Y. Gissel, AECD-2850, U. S. Atomic Energy Commission, Washington, D. C., Dec. 10, 1947

TABLE I-2[11]
Radioactive Isotopes of Phosphorus

Isotope	Methods of production	Type of decay	Decay product (stable isotope)	Half-life	Energy of β-rays (M e v)	Energy of γ-rays (M e v)	Chemical atomic weight
$_{15}P^{29}$	Si-p-n	β^+	$_{14}Si^{29}$	4 6 sec	3 6	1 28 (2 5%)	28 983
	Si-d-n					2 42 (0 5%)	
	P-γ-$2n$						
$_{15}P^{30}$	Al-α-n	β^+	$_{14}Si^{30}$	2 5 min	3 4		29 980
	Si-p-n						
	Si-^{3}He-p						
	P-n-$2n$						
	P-γ-n						
	S-d-α						
	Cl-γ-αn						
$_{15}P^{32}$	Si-d-γ	β^-	$_{16}S^{32}$	14 3 days	1 701 (100%)	None	31 975
	Si-α-p						
	Si-^{3}He-p						
	P-d-p						
	P-n-γ						
	S-n-p						
	S-d-α						
	Cl-n-α						
	Cl-γ-αn						
	Cl-d-$p\alpha$						
	Fe-high energy fission						
	Cu-high energy fission						
$_{15}P^{33}$	S-n-p	β	$_{16}S^{33}$	25 days	0 26 (100%)	None	—
	S-γ-p						
	Cl-γ-α						
	Cl-γ-$2p$						
$_{15}P^{34}$	S-n-p	β^-	$_{16}S^{34}$	12 5 sec	5 1 (75%) 3 2 (25%)	Present	—
	Cl-n-α						

at 120–140°C. under pressure. The molten sulfur phase is removed from the reactor, and the acid phase is filtered and treated with sodium hydroxide to remove corrosion products. After acidification with hydrogen chloride, the phosphate is precipitated with ferric or lanthanum chlorides to separate it from that radioactive sulfur which had been oxidized by the

nitric acid. The phosphate precipitate is then dissolved in hydrochloric acid and run through an ion-exchange column to remove the lanthanum or iron and other cations. After evaporation to dryness to volatilize the hydrogen chloride, the resulting phosphoric acid is redissolved in water and neutralized with sodium hydroxide before filtration through a sintered glass disk to remove any silica or foreign matter that might be present. The final solution contains about 0.5 millicurie per milliliter.

Phosphorus-32 has nearly ideal characteristics for tracer studies. Its beta radiation is sufficiently energetic so that any type of beta counting unit, including glass-walled Geiger-Müller tubes, can be used. Corrections for self-absorption are also seldom needed for thin samples having this energy radiation. Also, many studies can be carried out without making allowances for radioactive decay. Thus, in 1 hour 99.80% of the original activity is still present and in 24 hours 95.3% remains. Stock solutions can be stored for appreciable lengths of time, since the activity diminishes to $^1/_2$ in 2 weeks, $^1/_4$ in 1 month, and $^1/_{20}$ in 2 months.

ATOMIC STRUCTURE

Thus far, this discussion has been concerned with the various nuclei having a positive charge sufficient to exactly neutralize 15 electrons. According to the most recent concepts, the nucleus can be pictured as an exteriorly diffuse ball, about 10^{-12} cm. in radius. It is surrounded by a number of electrons, usually 18 (6 or 8 of which are shared) for the phosphorus atom in the normal ranges of temperature and pressure. These electrons are diffuse negative charges with essentially no mass. Since the radius of an atom can be shown from the packing in crystals to be equal to about 10^{-7} cm., there is well over a trillion times more vacant than filled space within the atom, with the mass essentially all concentrated in the nucleus. Since the nuclear quadrupole moment is zero for phosphorus, the charge distribution in the phosphorus nucleus is spherically symmetrical.

The nuclear radius reported above represents the radius in which most of the energy (or mass) of the nuclei is contained. However, quantum mechanical reasoning has shown that the elemental particles do not exhibit a discrete boundary but simply fade away into nothingness.

Orbitals

The usual discussion of the distribution of electrons about an atomic nucleus is based on concepts and notation specifically designed for the interpretation of spectrographic data. Thus, the basic states refer to isolated

atoms and their ions, such as occur in gaseous discharges, rather than to the chemically bonded atoms. According to this notation, the first stable electronic configuration is called the 1*s*-orbital, and two electrons with opposed

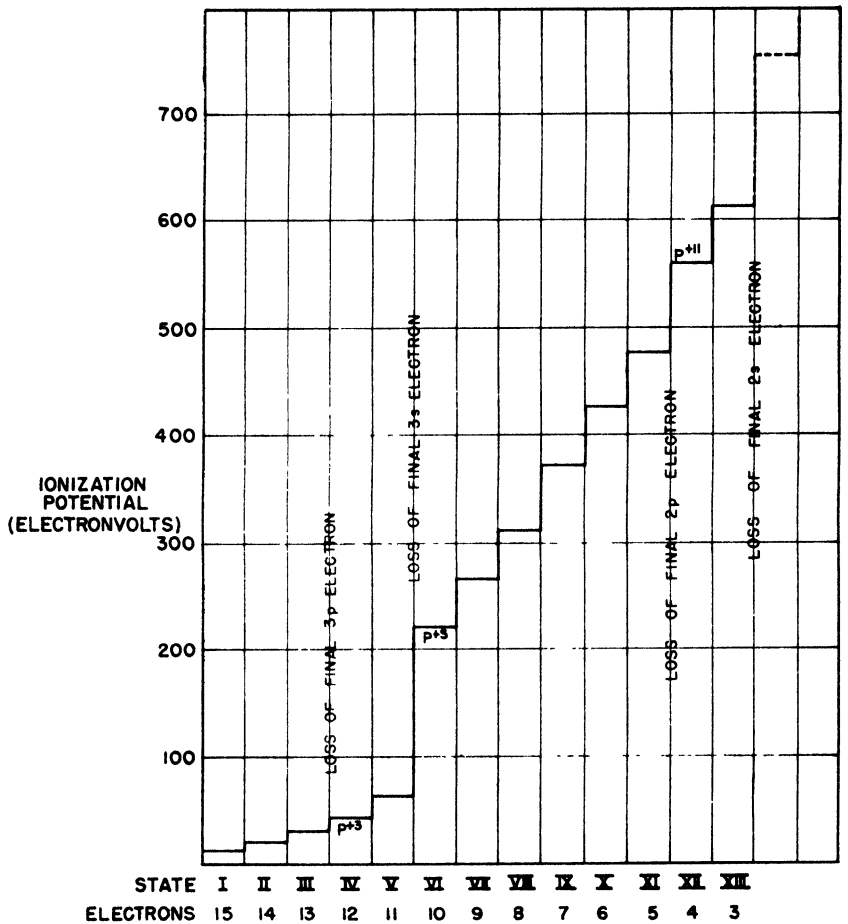


Fig 1-1. The successive ionization potentials of phosphorus. (1 e.v. = 23.06 kcal / mole)

spins fill this orbital to form a complete *K*-shell of electrons. The element helium exhibits an electronic structure corresponding to a completed *K*-shell. The next outer shell of electrons is called the *L*-shell and is filled by a pair of electrons in the 2*s*-orbital and three pairs of electrons in the 2*p*-

orbital. A completed *L*-shell of eight electrons is found for the inert gas, neon. The *M*-shell contains one electron pair in the 3*s*-orbital, three pairs in the 3*p*-orbital, and five pairs in the 3*d*-orbital. Argon corresponds to a filling of the 3*s*- and 3*p*-orbitals, with the 3*d*-orbitals left vacant.

The electronic configuration for the neutral phosphorus atom is $1s^2 2s^2 2p^6 3s^2 3p^3$, where the superscripts refer to the number of electrons in each orbital. These superscripts add up to 15. The ionization potential, representing the work necessary to remove an electron from the atom, is shown for 13 successive ionization stages of phosphorus in Figure 1-1. In this figure, it should be noted that the energy to remove an electron increases as the degree of ionization of the phosphorus becomes greater. This increase occurs in a gradual stepwise manner within an orbital, but at the end of each orbital there is a noticeably larger increase in the energy, showing the stability of a completed orbital. These large increases come for the P^{3-} ion with a $1s^2 2s^2 2p^6 3s^2$ configuration, the P^{5-} ion with a $1s^2 2s^2 2p^6$ configuration (completed *L*-shell $\approx$ neon-type structure), and the P^{11-} ion with a $1s^2 2s^2$ configuration.

Spectra

The ionization potentials discussed above were calculated from the limiting wave numbers obtained from spectral terms. Although a large number of terms have been reported for the phosphorus spectrum, a complete assignment has not yet been made for any of the ionization stages of phosphorus.[13] In Figure 1-2, the energy levels of the un-ionized phosphorus atom are plotted in order to give an idea of the differences in energy between the various electronic configurations. The arrows in this figure do not refer to allowed spectrographic transitions but merely show the over-all change in electronic configuration between the various groups of energy levels and the ground state.

As compared to the common metals, 10 to 1000 times as much phosphorus must be present in order to be detected under the conditions usually employed in emission spectroscopy.[14] The four sensitive lines used in spectrographic analysis are in the near ultraviolet at 2535.65, 2553.28, 2534.01, and 2554.93 A. All of these lines belong to the phosphorus I spectrum and hence are associated with the electronic transitions in the un-ionized or neutral atom. The lines are listed above in order of their sen-

[13] C. E. Moore, "Atomic Energy Levels," *Natl Bur Standards Circ.* 467, Vol. I, 163-80 (1949).

[14] C. E. Harvey, *Method of Semi-Quantitative Spectroscopic Analysis*, Applied Research Laboratories, Glendale, California, 1947.

sitivities, which also turns out to be the order of their arc and spark intensities By emission spectroscopy, phosphorus can readily be detected in the range of about 0.1-1% concentration in a matrix of other materials, the exact limit of detectability being dependent on the composition of the matrix[14] and the chemical combination of the phosphorus

The x-ray spectra of the elements correspond to transitions in the inner shells of electrons—the K and L shells for phosphorus. It is generally the

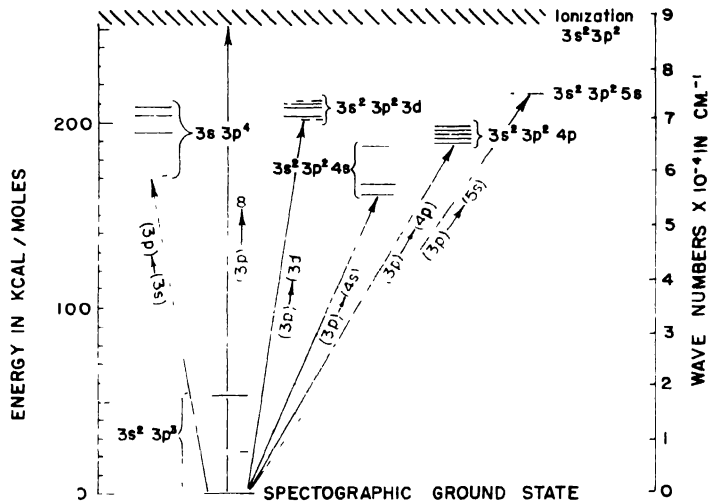


Fig 1-2 Energy levels of the un-ionized phosphorus atom from the P-I spectrum

case for elements of lower atomic number that the transitions in the inner shells are slightly affected by the electronic configurations in the valence shell of electrons, *i.e.*, the M shell for phosphorus Thus, the critical absorption edge for the K line of phosphorus atoms which are bonded to three neighboring atoms occurs at 5 77 A , whereas the absorption edge for phosphorus which is bonded to four neighboring atoms is found at about 5.75–5.76 A.[15] Differences between the x-ray spectra of individual compounds in either class were also noted.

Chemical Combination of Atoms

Atomic spectra, as exemplified by the data of Figure 1-1, support the view that the inert-gas type of electronic configuration exhibits exceptional

[15] O. Stelling, *Z anorg. u. allgem. Chem.*, **131**, 48 (1923). For temperature dependence, see H. W B Skinner, *Trans Roy Soc (London)*, **A239**, 95 (1940)

stability. In a large number of chemical combinations, especially for elements in the second row of the periodic table, the constituent atoms have an electronic configuration of the inert-gas type. In general, this type of configuration can be achieved in two ways: (1) by transfer of the outermost electrons from one atom to another and (2) by sharing of these outermost electrons between atoms. The transfer of an electron from one neutral atom to another results in the donor atom becoming positively charged and the acceptor atom becoming negatively charged. Thus, both atoms are ionized and attract each other electrostatically. The sharing of electrons between two atoms results in what is usually called in America a covalent bond. Although covalent bonds in which the binding is effected by one and by three electrons are known for stable molecules in a few exceptional cases (*e.g.*, O_2, NO, NO_2, OF, and ClO_2), the usual covalent single bond is composed of an electron pair. Multiple bonds consist of several pairs of electrons (thus, C=C is equivalent to C::C and C≡Cis equivalent to C:::C).

It should be noted that bonds can be intermediate in type between the completely ionic ones and the covalent ones in which the bonding electrons are equally shared. In such intermediate bonds, the bonding electrons are more closely associated with one of the bonded atoms than with the other. Hence, one of the atoms is negatively charged and the other positively. These charges can have any fractional value, not being limited to discrete numbers of electrons. Naturally, the exact polarity of such an intermediate bond must depend to some extent on the environment of the atoms. In general, only the weaker bonds (those with low binding energy) change their character appreciably with their environment. The bonds intermediate between the purely ionic and the purely covalent ought to be called polar bonds, as compared to the term nonpolar for those bonds possessing only very slight ionic character. Unfortunately, the term polarity has been used in other connotations in the scientific literature and thus probably should be avoided.

In some of the literature, completely ionized atoms are said to exhibit polar bonds. Also, the concept of formal charge on an atom and the unfruitful idea of semipolar bonds (see p. 86), which are defined as those bonds in which both electrons can formally be attributed to the same neutral atom, confuse the issue.

An uncontroversial way of saying the same thing is to speak of the ionic character of covalent bonds. It should be noted that a bond intermediate between an ionic and a covalent type of structure is only possible when the same number of paired and unpaired electrons are involved in the completely ionic and completely covalent limiting structures.

Directional Characteristics of Orbitals

In the next chapter, the concept of chemical binding will be explored quantitatively, with especial emphasis on the compounds of phosphorus. Meanwhile, the general question of the electronic configurations about atomic nuclei will be considered. It can be shown that *s*-orbitals exhibit spherical symmetry, whereas the three *p*-orbitals are directed at right angles to each other. The five *d*-orbitals are also directed, forming a pentagonal pyramid with its apex at the atomic nucleus. Chemical bonds are created by the overlapping of the atomic orbitals, with the word "overlapping" signifying the coincidence of the regions in space in which the two bonded atoms have high electron densities. This means that *p*-bonds tend to be directed at right angles to each other, and that *s*-bonds are not directed.

Directed Bonds

Both pure *p*- and pure *s*-bonds are found in chemical compounds, but pure *d*-bonds are never found as such. This is because of the process of hybridization in which the orbitals which are stable in isolated atoms combine together to give new orbitals which are stable in molecules. Thus, *s*-electrons and *p*-electrons can hybridize in a number of ways, of which the best known are (1) the *sp*-orbital with a linear configuration, (2) an sp^2-orbital with three-fold symmetry having axes arranged at 120° to each other in a plane, and (3) an sp^3-orbital with tetrahedral symmetry. There are also a number of hybrid orbitals between *d*- and *s*- and/or *p*-electrons.

Since simple chemical bonds (single bonds, otherwise known as σ-bonds) are formed by overlapping of atomic orbitals in the direction of high electron density, the chemical bonds from a given atom will exhibit the directional characteristics of the pure or hybridized electronic orbital of the valence electrons, which, by the way, must all be in the same orbital. In the case of phosphorus, it appears that the directional characteristics can be approximated rather closely by five hybrids, which are dubbed the "σ-bond base structures" throughout this book. These hybrids and their corresponding bonds are (1) *p* (a single bond in phosphorus-based diatomic molecules), (2) p^3 with some sp^3 character (three σ-bonds at right angles to each other for the pure p^3-hybrid), (3) sp^3 (four σ-bonds pointing toward the apices of a tetrahedron), (4) sp^3d (five σ-bonds pointing toward the apices of a trigonal bipyramid), and (5) sp^3d^2 (six σ-bonds pointing toward the apices of an octahedron). Although there may be an appreciable amount of *d*-character in the σ-bond hybrid of a phosphorus atom bonded to four neighboring atoms, the geometry and many other properties correspond with

sufficient closeness to those predicted for an sp^3-hybrid so that this hybrid can be used as a prototype for all of the compounds in which the phosphorus is connected to four neighboring atoms. Indeed, it is quite generally found that hybrid bonds in which there are noninteger contributions of

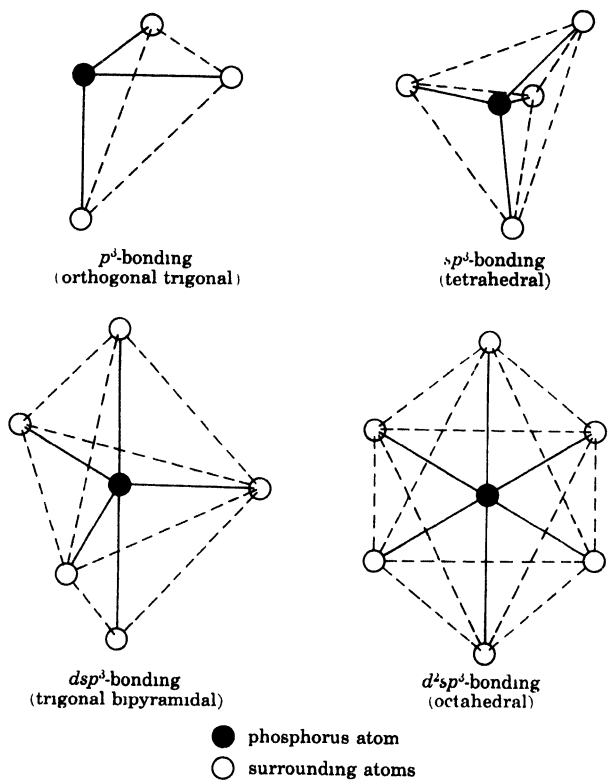


Fig 1-3. Geometry of the various types of bonding found in the compounds of phosphorus The black balls represent the phosphorus and the white balls the atoms to which it is bonded.

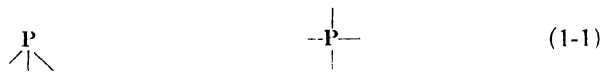
s-, *p*-, and *d*-electrons show the gross directional characteristics of the nearest integer-based hybrids. The geometry of p^3, sp^3, sp^3d, and sp^3d^2-hybrids are represented schematically in Figure 1-3.

The bond types are all named on the tacit assumption that one electron in each electron pair making up a bond comes from one bonded atom and the other electron from the other bonded atom. There are cases, however,

where both electrons in a bond come from one atom -the electron donor- and are shared by the other atom—the electron acceptor. Such a case is found in the sp^3-bonds of the phosphorus atom, which in its spectrographic ground state has two s- and three p-electrons, one more electron than is shown in the sp^3-hybrid notation. Since electrons are indistinguishable from one another, it makes no difference from which atom they come; and an atom exhibiting sp^3-hybridization, for example, has the same general electronic configuration no matter from whence the four pairs of shared electrons came.

Number of Valence Electrons

In the triply connected phosphorus compounds in which the phosphorus atom exhibits predominantly p^3-bonding, there is a pair of electrons in the $3s$-orbital and three pairs of electrons in the $3p$-orbital, three of which electrons come from the phosphorus and three from the neighboring atoms to which the phosphorus atom in question is linked. In the tetrahedrally connected phosphorus compounds, the total of eight valence-shell electrons (four electron pairs) come from the five valence electrons of the phosphorus plus three electrons contributed by the neighboring atoms. Both the triply and tetrahedrally connected phosphorus compounds in their simplest representation (only σ-bonds) follow the Octet Rule with respect to the phosphorus, as this atom is surrounded by eight electrons in the valence shell, as shown below.



(1-1)

where the dashes stand for electron-pair bonds.

In the sp^3d- and sp^3d^2-structures, the Octet Rule is violated, since there are ten and twelve electrons, respectively, in the σ-bond valence shell of the phosphorus atom. In the M- (or 3) shell of electrons, the d-electrons have a very high energy, about 200 kcal./mole being needed to promote a $3p$-electron of phosphorus into the $3d$-orbital according to Fig. 1-2.

An example of the high energy of the $3d$-level is found in the sequence of elements in the periodic table. Thus, when the p-orbitals in the L-shell are filled at the argon atom (configuration: $1s^22s^22p^63s^23p^6$), the succeeding two atoms (K and Ca) have electronic configurations corresponding to filling of the $4s$-orbital (K: $1s^22s^22p^63s^23p^64s$; Ca: $1s^22s^22p^63s^23p^64s^2$)

Even though the hybrid orbital has a lower energy in the chemical compound in which it appears than the energy of the spectrographic-type (s, p, d) orbitals from which it was constructed, hybrids involving d-orbitals

are generally believed to be unstable relative to those in which just *s*- and *p*-orbitals are involved for elements, such as phosphorus, in the second row of the periodic table. This means that there should be only a restricted number of compounds of phosphorus in which *d*-orbitals play a major role. And, in fact, there seem to be only a few structures of this type which have been prepared so far. These are the pentahalides and pentaphenyl phosphorus in which the phosphorus shows five bonds (sp^3d) and the hexafluorophosphate and hexachlorophosphate* ions in which the phosphorus atom shows six bonds (sp^3d^2). Diffraction data on the pentahalides support the sp^3d-hybridization, since the halides are arranged at the apices of a trigonal bipyramid. The data on the $(PCl_6)^-$ ion show the chlorine atoms to be octahedrally arranged about the phosphorus as predicted for sp^3d^2-hybridization. Although the geometry of these structures is in accord with hybrids involving *d*-electrons, the bonds exhibit considerable ionic character in order to reduce the energy requirements of using the *d*-electrons.

Bond Angles

There are a large number of phosphorus compounds in which the phosphorus is triply and tetrahedrally connected to neighboring atoms. In the triply connected phosphorus compounds, there is some tendency for the nonbonding pair of *s*-electrons to hybridize with the three pairs of *p*-electrons involved in the chemical bonds. This means that the triply connected phosphorus compounds should exhibit bond angles which range from the 90° angle for p^3-bonding to 109°28′, the tetrahedral angle for sp^3-bonding. As can be seen from Table 1-3, this is the case for all of the triply connected phosphorus compounds excepting the P_4 molecule. This latter molecule is said to have bent bonds. The term "bent" is used because it is believed that the *p*-orbitals in these bonds do not overlap head-on but do so at an angle. This puts the P_4 molecule in the same class as cyclopropane, cyclobutane, and ethylene oxide, in which the small-membered rings cause considerable strain (appearing as bent bonds). In the P_4 molecule there are four fused three-membered rings.

The bond angles in nearly all of the tetrahedrally connected phosphorus compounds are close to the 109°28′ angle corresponding to sp^3-bonding, as can be seen in Table 1-3. Deviations from this angle will be discussed in the chapters concerned with the chemistry of each particular compound. In general, it can be said that the deviations are due to steric hindrance, electrostatic repulsions, and effects involved in multiple bonding.

* Crystalline PCl_5 has the structure: $(PCl_4)^+(PCl_6)^-$. However, the $(PCl_6)^-$ is not otherwise known and is not stable in solution.

TABLE 1-3
Bond Angles to the Phosphorus in Various Compounds

Triply linked phosphorus			Tetrahedrally linked phosphorus		
Compound	Angle	Size	Compound	Angle	Size
Theory	(p^3-sp^3)	90° 109 5°	Theory	(sp^3)	109 5°
PH	HPH	93 7° ± 0 5°	PO_4^{3-}	OPO	109° ± 1 3°
PF	FPF	104° ± 3°	P_4O_{10}	O_aPO_b	116 5 ± 1°
				O_bPO_b	101 5 ± 1°
$PFCl_2$	FPCl	102° ± 3°			
	ClPCl				
PCl_3	ClPCl	100 5° ± 1 5°	$(PNCl_2)_3$	NPCl	109° ± 3°
PBr_3	BrPBr	101 5° ± 1 5°	$(PNCl_2)_4$	NPCl	105 5° ± 1°
PI	IPI	102° ± 2°	POF	FPF	107° ± 2°
					102 5° ± 2°
P_4	PPP	60°	$POFCl_2$	ClPF	106° ± 3°
				ClPCl	
Black P	PPP	96° 103 5°[b]	POCl	ClPCl	106° ± 1°
					103 6° ± 2°
P_4O_6	OPO	99° ± 3	POBr	BrPBr	108° ± 3°
			PSF_3	FPF	100 3° ± 2°
					99 5° ± 2°
				FPS	118° ± 2°
			PSCl	ClPCl	100 5° ± 1°
			PSF_2Br	FPBr	106° ± 3°
			$PSFBr_2$	BrPBr	100° ± 3°
			$PSBr_3$	BrPBr	106° ± 3°

[a] Where O_b = bridging oxygen, and O_a = apical oxygen

[b] 99° in the plane of the cleavage layer and 103 5° for the bond at an angle to this plane in crystalline black phosphorus In the amorphous variety, the bond angle is 96°

Multiple Bonds

According to the molecular orbital theory, colinear overlapping of atomic orbitals results in single bonds which in themselves are symmetrical.

Two different approximation methods have been developed to discuss chemical bonding. One of them, the valence bond method, describes the combination of atoms to form molecules in terms of the orbitals derived from the isolated atoms. The other approach, the molecular orbital method, considers the nuclei of the final molecule to be in place and to create a field in which the electrons must move. The state of the molecule is then described in terms of the permitted energy levels or orbitals of the electrons in the field of the nuclei. Since the two methods involve different approximations, the results of calculation will in general differ, although qualitative conclusions will agree. Throughout this book the terminology of either valence bond or molecular orbital treatments

will be employed interchangeably, depending upon which approximation is more suitable for the particular discussion

These single bonds are called σ-bonds and always occur when s-orbitals combine with any other type of orbital to form a bond. They also occur when p- or d-orbitals or hybridized orbitals combine end-on In addition to

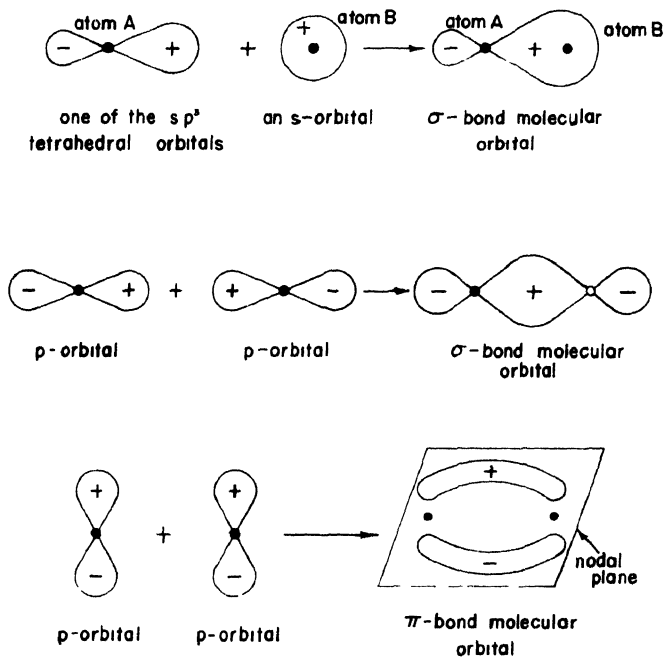


Fig. 1-4. Diagrammatic representation of the formation of σ- and π-bonds. The black dots represent the atomic nuclei, and the encircled areas are regions of high charge density of the respective orbitals

the σ-bonds, there are π-bonds which tend to be geometrically concentrated so that the greatest electron density lies on a plane between the two bonded atoms. Such π-bonds are formed when p- and/or d-orbitals, which are not spherically symmetrical, overlap sideways. An approximate representation of the formation of σ- and π-bonds is presented in Figure 1-4. Because of their shape, Coulson has called the σ-bond orbitals "sausage orbitals" and the π-bond orbitals "double streamer orbitals." By leaving out the σ-bond sausage orbital and only showing its axis and also only showing the nodal plane of the π-bonds and not the streamers, the geometry

of several multiply bonded compounds is shown in Figure 1-5 In all cases, the first electron pair which bonds two atoms together appears in the form of a σ-bond, whereas subsequent bonds, such as are found in the multiply bonded organic compounds like benzene and ethylene, are of the π-type.

As will be demonstrated quantitatively in the next chapter, the tetrahedrally connected phosphorus compounds show a considerable amount of

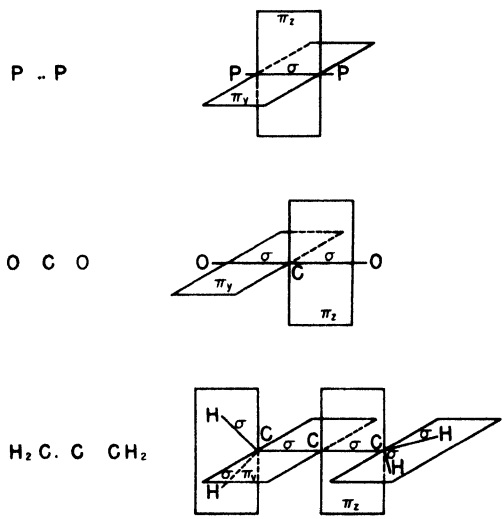


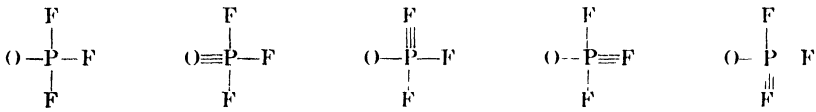
Fig 1-5. Geometry of several multiply bonded compounds, showing the σ-bond axes and the nodal planes of the π-bonds

π-bond character. The structure of such multiply bonded compounds is difficult to represent by the customary chemical formulas. It is easiest to think of the over-all structure as a superimposition of a number of structures.

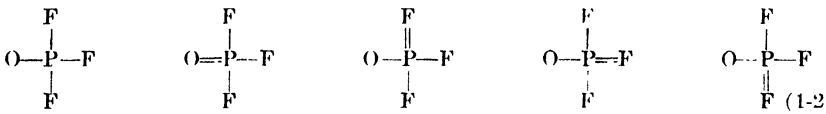
It must be emphasized that this pictorial representation does not give anywhere near an exact description of the molecule. The pictures should be interpreted as a graphical rendering of the structures associated with terms in an expansion of the unknown wave equation as an infinite series, employing only those terms which represent structures that are felt to have reasonable energies and which can be presented pictorially using the convention of bonds developed by organic chemists prior to the advent of quantum mechanics. It should be noted that the wave equation for the ground state of the hydrogen atom can be expressed as an infinite series involving the complete solution for the particle in a box (a Fourier series expansion). Obviously, the hydrogen atom does not

resonate in a physical sense between the various stationary states of a particle in a box and, likewise, a molecule does not have one structure part of the time and another at other times.

This approach can be used mathematically as well as pictorially; and, in the language of the atomic orbital method of computing molecular structures, the superimposition is called a resonance hybrid. The real structure of the POF_3 molecule, for example, appears to be a combination of the following structures

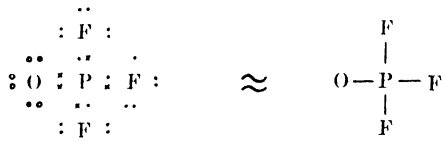


or perhaps



(1-2)

The Octet Rule predicts the structure exhibiting four single bonds, as shown by the following electronic representation in which the electrons contributed by the phosphorus are denoted by crosses, x, the electrons from the oxygen by small circles, °, and the electrons from the fluorine atoms by dots, •.



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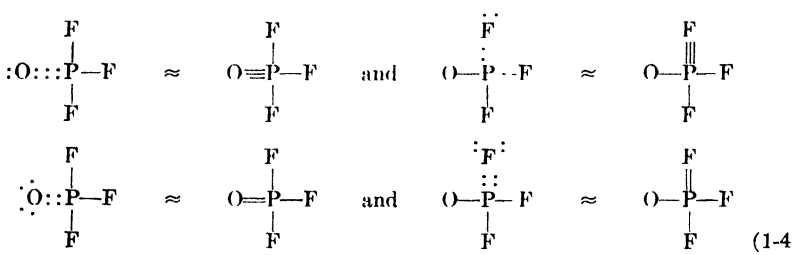
The multiple bonds are formed by sharing with the phosphorus electron pairs on the fluorine or oxygen, electron pairs which were not previously shared. This is shown by the following diagrams in which all electrons are represented by dots, and a line is an electron pair bond:



(1-4)

SUMMARY

1. Phosphorus has only one stable isotope, $_{15}P^{31}$, and five radioactive isotopes of which $_{15}P^{32}$, with a half-life of 14.3 days, is used in tracer studies.

2. Phosphorus is the least abundant of the elements in the second row of the periodic table, being present to 1.3% of the amount of silicon in the universe.

3. The chemical shifts in the nuclear magnetic resonance spectrum of phosphorus are readily measured and afford an interesting new method for studying the bonding types found in phosphorus compounds.

4. In emission spectrography, phosphorus can be readily detected in the range of about 0.1–1%, depending on the other materials present.

5. The directional characteristics of phosphorus in its compounds correspond to p^3-, sp^3-, sp^3d-, and sp^3d^2-bonding, with all but a small number of the compounds exhibiting the geometry of p^3- and especially sp^3-bonding.

6. The bond angles in the P_4 molecule are unusually small, being 60°. The regular geometry of this structure leads to the formation of bent bonds, such as are found in cyclopropane.

7. π-Bonding is qualitatively described, and the hypothetical resonance structures corresponding to multiple bonding in the tetrahedrally connected phosphorus compounds are depicted.

CHAPTER 2

Interaction Between Atoms, with Especial Reference to Phosphorus Chemistry

THE PERIODIC TABLE

Spectrographic studies[1] have shown that the ground states of the un-ionized atoms of the various chemical elements have the electronic configurations shown in Table 2-1. On the basis of these ground-state configurations, the elements can be divided into the usual chemical classifications of the periodic table. The inert gases have completely filled *s*- and *p*-orbitals in their ground state. The main sequence or representative elements, which include the elements in the first two rows of the periodic table, correspond to the filling of the *s*- and *p*-orbitals, whereas the subgroup and outer-transition elements correspond to the filling of the *d*-orbitals. The inner-transition elements are obtained by filling the 4*f*- and 5*f*-orbitals.

By a simple rearrangement, the tabulation of Table 2-1 can be converted into a long-form periodic table, an example of which is given in Figure 2-1. A long-form version of the periodic table consists of an arrangement of all the chemical elements except the inner-transition elements into rows starting or ending with the inert gases, the elements being taken in the order of their atomic numbers. This version of the periodic table shows the close relationship between the arrangement of the electrons in the isolated atom and the over-all chemical properties of the element.

Historically the periodic table was developed to show the family relationships among the elements. It was used, for example, to emphasize the close similarities and gradations in the compositions and properties of the compounds of the Group V elements: nitrogen, phosphorus, arsenic, antimony, and bismuth. In addition to the gradations within a group, the similarities between the compounds of elements within a row (*e.g.*, silicon, phosphorus, and sulfur) and at an angle (*e.g.*, carbon as compared to phos-

[1] C. E. Moore, "Atomic Energy Levels," *Natl. Bur. Standards, Circ.* 467, Vol. I (1949).

TABLE 2-1
Classification of the Elements by the Electronic Configuration in the Ground State

Inner electronic configuration (electrons below the valence shell)	Shell being filled (valence shell)	Highest level filled in the valence shell			
		s-Orbital (2 electrons)	*p*-Orbital (6 electrons)	*d*-Orbital (10 electrons)	*f*-Orbital (14 electrons)
None	1 *s*	H, He			
$1s^2$	2 *s* and *p*	Li, Be	B, C, N, O, F, Ne		
$1s^22s^22p^6$	3 *s* and *p*	Na, Mg	Al, Si, P, S, Cl, A		
$1s^22s^22p^63s^23p^6$	4 *s*	K, Ca			
$1s^22s^22p^63s^23p^6$	3 *d*			Sc, Ti, V, Cr, Mn, Fe, Co, Ni	
$1s^22s^22p^63s^23p^23d^{10}$	4 *s* and *p*	Cu, Zn	Ga, Ge, As, Se, Br, Kr		
$1s^2 .3d^{10}4s^24p^6$	5 *s*	Rb, Sr			
$1s^2. 3d^{10}4s^24p^6$	4 *d*			Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd	
$1s^2 4s^24p^64d^{10}$	5 *s* and *p*	Ag, Cd	In, Sn, Sb, Te, I, Xe		
$1s^2. 4d^{10}5s^25p^6$	6 *s*	Cs, Ba			
$1s^2. .4d^{10}5s^25p^6$	5 *d*			La	
$1s^2. ..4d^{10}5s^25p^6$	4 *f*				Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb
$1s^2. . 4f^{14}5s^25p^6$	5 *d*			Lu, Hf, Ta, W, Re, Os, Ir, Pt	
$1s^2. 5s^25p^65d^{10}$	6 *s* and *p*	Au, Hg,	Tl, Pb, Bi, Po, At, Rn		
$1s^2. 5d^{10}6s^26p^6$	7 *s*	Fr, Ra			
$1s^2. 6s^26p^67s^2$	6 *d*			Ac	
$1s^2 6s^26p^67s^2$	5 *f*				Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf ( ) ( )

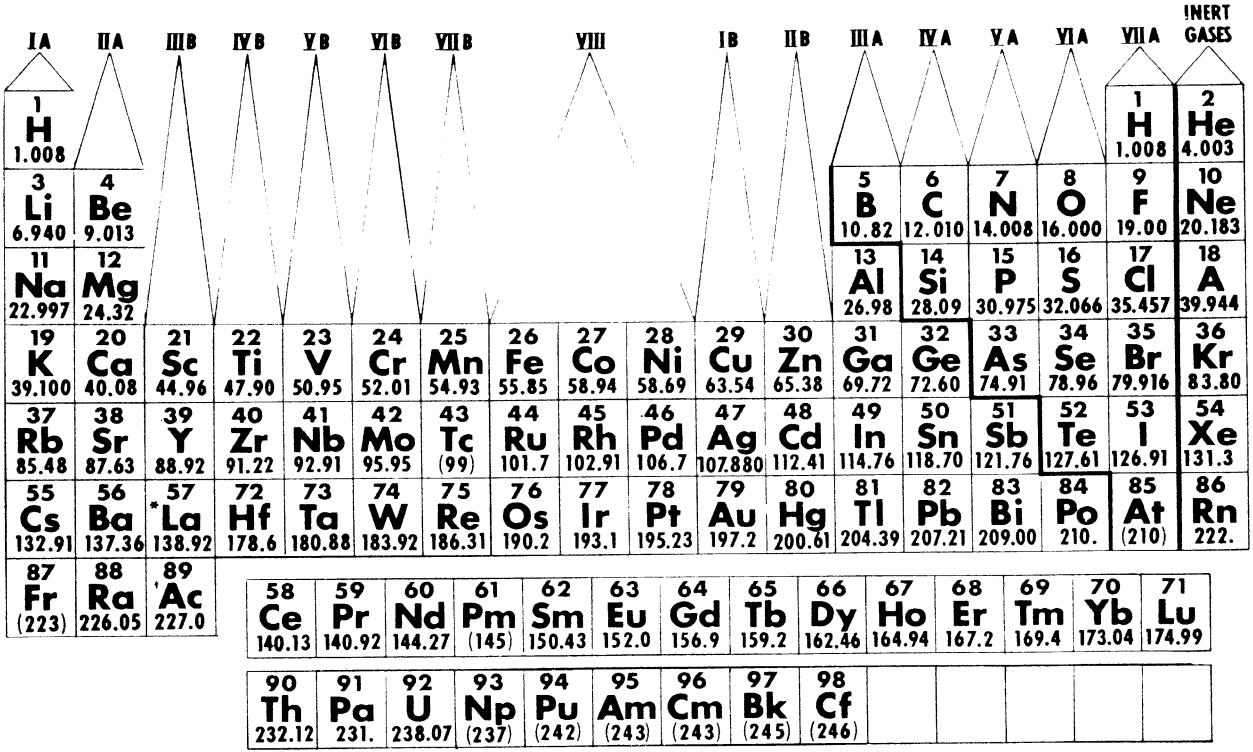


Fig. 2-1. A long-form periodic table. *Lanthanum series. +Actinium series. Numbers in parentheses indicate mass number of most stable known isotope. Atomic weights are 1952 international committee values. Elements 99, fermium (Fm), and 100, mendelevium (Mv), are not shown.

phorus) became apparent * The fact that interpretation of atomic spectra in terms of electronic configuration correlates so nicely with the general scheme of chemical interrelationships exemplified by the periodic table is a major proof of the concept that the number and behavior of the extranuclear electrons, especially the outermost electrons, of an atom determines its chemical properties.

Periodic Variation of Electronegativities and Ionization

The ability of atoms to attract and hold electrons in their valence shell decreases from top to bottom and from right to left in the period table.

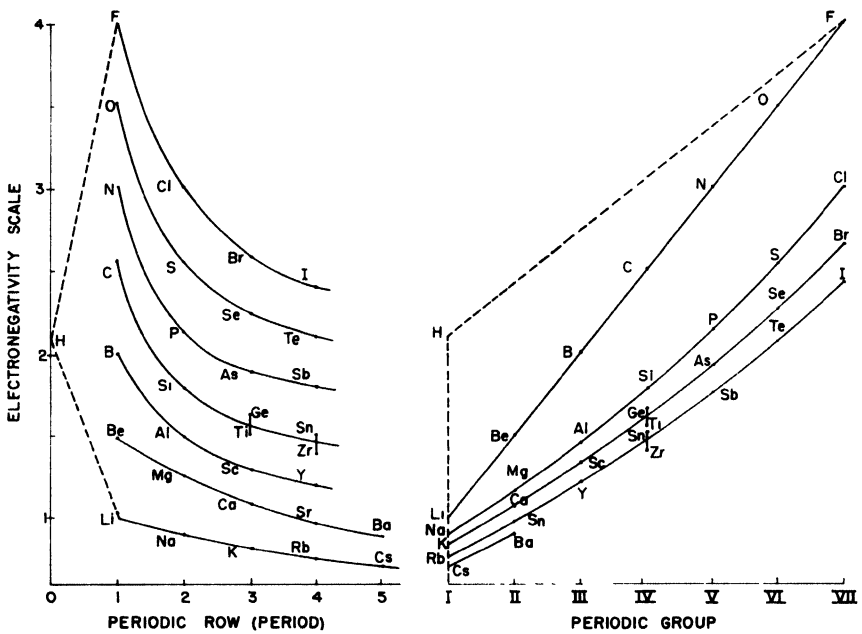


Fig. 2-2 Approximate values of electronegativities on Pauling's scale as a function of placement of the elements in the periodic table

This ability, called electronegativity, is thus at a maximum for fluorine and at a minimum for francium, the heaviest alkali metal. The concept of electronegativity has been put onto a quantitative basis by Pauling[2] and

* For further detailed information about the relationships between the elements see a good text on general inorganic chemistry, such as ref 4

[2] L. Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932), *The Nature of the Chemical Bond* 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 58–69.

others. Pauling's method for defining electronegativities from thermodynamic data is discussed in detail later in this chapter (p. 30). A graph of electronegativity values of the common elements as a function of their position in the periodic table is given in Figure 2-2. As might be expected, the division of the elements into metals, metalloids, and nonmetals can be done on the basis of electronegativity values. Thus, the metallic elements are seen to have electronegativities below about 1.5 on Pauling's scale, whereas the metalloids lie in the electronegativity range of 1.5–2.0, and the nonmetals have electronegativities greater than about 2.0. Even though the electronegativity scale is primarily designed for treating individual chemical bonds, a number of interesting correlations have been developed between electronegativity and gross chemical properties, such as acid-base strength[3] and hydride type.[4]

Ionization of Atoms as Function of Periodic Placement

Although large oxidation numbers of 4, 5, and even 6 are ascribed to elements of high atomic number, such as uranium, there is no question but that these oxidation numbers do not correspond to the charge borne on the ionized atom but, instead, refer to covalently bound atoms which bear only a small charge usually less than ± 2 electrons. Spectrographic data show that the ionization potentials are very high for all triply charged positive ions. The lowest ionization potentials for the formation of ions having a + 3 charge from the neutral monatomic gas are found for the Group III metals. These potentials are 876 kcal /mole for B^{3+}, 656 kcal./mole for Al^{3+}, 572 kcal./mole for Sc^{3+}, and 464 kcal./mole for Y^{3+}. From this type of data and other reasoning, one can conclude that triply and quadruply charged ions can only be formed by elements of very large atomic number, if they are formed at all under normal chemical conditions. This concept that individual atoms can only exhibit small charges was first stated by Pauling[5] as the "principle of electroneutrality."

Under normal chemical conditions (temperature below about 1000°C.), most of the elements in the periodic table can form ions (*i.e.*, the atom in question can bear an electrical charge that is not neutralized by opposite charges on neighboring atoms to which the first atom is covalently bonded). However, there is considerable evidence to show that boron, carbon, sili-

[3] F. Gallais, *Bull. soc chim France*, **14**, No 5, 425 (1947).

[4] T Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1952, pp 405–06

[5] L. Pauling, *J Chem Soc*, **1948**, 1461 (1948), *Victor Henri Memorial Volume*, Maison Desser, Liége, Belgium, 1948

con, and phosphorus atoms seldom, if ever, bear an appreciable charge in their stable compounds. These elements have intermediate electronegativities (1.8–2.6) and, moreover, lie midway between the stable electronic configurations corresponding to the inert gases, so that complete ionization would lead to unconscionably high charges. Naturally, elements for which the electronegativities are neither high nor low have the best possibility for sharing electrons with other elements without either completely losing or capturing the electrons. The elements which lie close in the periodic table to the four elements listed above also tend to approximate closely the covalent-bond model in most of their compounds.

The nonexistence of ionized phosphorus in solutions, solids, and probably in melts is substantiated by the ionization potentials shown in Figure 1-1. Two hypothetical ionic species of phosphorus which are often discussed in the early or less precise scientific literature are the P^{3+} and P^{5+} ions. However, these ions have the extremely high gas-phase ionization potentials of 697 and 1500 kcal./mole, respectively, as compared to 119 kcal./mole for Na^{+} and 274 kcal /mole for Ca^{2+} Since the heats of chemical reactions are usually less than a few hundred kcal./mole, there appears to be no mechanism whereby the highly charged ions such as P^{3+} and P^{5+} can be stabilized in any environment

Proof that phosphorus is covalently bonded to its neighboring atoms is given by complete x-ray analyses[6] in which detailed electron density projections have been calculated. From these electron density maps, it can be seen that the electrons are shared between each phosphorus atom and its four neighboring oxygen atoms in the phosphates. The existence of indirect spin-spin splitting[7] in the nuclear magnetic resonance spectra of a number of phosphorus compounds also proves that phosphorus is covalently bonded to its neighboring atoms in these structures. As explained in a later section of this chapter, indirect spin-spin splitting occurs when the coupled nuclei, each exhibiting a spin, are so arranged that the same electrons circle all of them. In other words, the coupled nuclei are held together by covalent bonds. Indirect spin-spin splitting has been observed for a variety of compounds in which the phosphorus atoms are bonded to 3, 4, 5, and 6 neighboring atoms. A third proof that phosphorus is covalently bonded to its neighboring atoms is found in the $n \rightarrow \pi^*$ spectrographic

[6] See, for example, C. Romers, J. A A. Ketelaar, and C. H MacGillavry, *Acta Cryst.*, **4**, 114 (1951); and S. Furberg, *Acta Chem. Scand.*, **9**, 1557 (1955).

[7] C. F. Callis, J R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2719 (1957).

transition.[8] The lowest energy transitions in many molecular species are of this type, corresponding to the formation of an antibonding π-orbital from a nonbonding orbital.

Atomic Radii as Function of Atomic Number

In addition to the factors discussed above, the radii of the atoms also play an important role in determining chemical structures. In Figure 2-3,

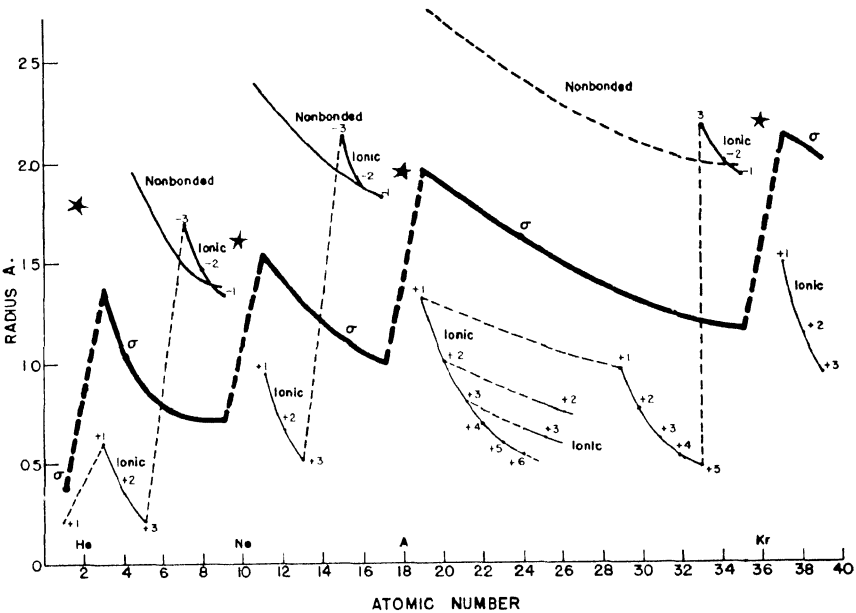


Fig. 2-3. Various atomic radii plotted as a function of atomic number to show the periodicity. Stars represent nonbonded radii of inert gases

the various kinds of atomic radii are plotted as a function of atomic number for the elements in the first three rows of the periodic table. In this graph, the closest-packing radii of the inert-gas atoms are denoted by a star. It is seen that the σ-bond radii decrease appreciably when going from the left to the right in each row of the periodic table, and, as might be expected, the σ-bond radii in each successive row in the periodic table are larger than the

[8] S. P. McGlynn and M. Kasha, *Molecular Quantum Mechanics Conference*, Univ. of Texas, Austin, Texas, National Science Foundation, Dec. 1955, Session IV, p. 25; L. Goodman and H. Shull, *J. Chem. Phys.*, **22**, 1138 (1954).

radii in the preceding row The ionic radii (some of which are hypothetical) are also given, and it will be noted that the positive ions are considerably smaller than the same atoms when σ-bonded, the positive ions of one row being of the order of magnitude in size of the σ-bonded atoms of the preceding row. For negative ions, the reverse effect is true, and the negative ions are of the order of size of the σ-bonded atoms of the succeeding row. It is also interesting to note that the nonbonded atomic radii are approximately the same size as the radii of the negative ions As demonstrated by the estimated values given for the transition metals—manganese, iron, cobalt, nickel, and copper—the greater the charge on a cation, the smaller its radius

Since the decrease in size when going from σ-bonded atoms to the respective positive ions is approximately equal to the increase in size when going from the σ-bonded atoms to the respective negative ions, a given internuclear distance when calculated for a pair of ions will be about the same as the distance calculated for covalent bonding of these same atoms. Early workers in the field of crystal structure thus were able to approximate closely the observed internuclear distances by sets of ionic radii which included such unlikely ions as I^{5+} and S^{6+}. Although some radii for ions having charges equal to or greater than three are shown in Figure 2-2, it should be remembered that such highly charged ions are probably not to be found in appreciable amounts in any chemical system at or below normal temperatures

BOND ENERGIES

Following Pauling, we designate as "bond energies" quantities which are not strictly internal energies but contributions of the bonds to the heats of formation (enthalpies) of molecules containing them, when the molecules are considered as being formed from the constituent atoms in the form of monatomic gases in their spectrographic ground states. Since the usual standard states employed in thermodynamics often correspond to considerable molecular complexity, the spectrographic ground states have been chosen as the simplest readily available reference points, even though for some theoretical purposes it would be more ideal to measure the energy from the gaseous atom in its electronic configuration (usually nonexistent *per se*) corresponding to the appropriate type of bonding.

As an example, the energy of the P—H bond in phosphine is calculated as follows.

$^1/_2H_2(g) + {}^1/_4P_4(c) \rightarrow PH_3(g)$ $\Delta H = +2\ 21$ kcal
$^1/_2H_2(g) \rightarrow H(g)\ (^2S_{1/2})$ $\Delta H = +52\ 09$
$^1/_4P_4(c) \rightarrow P(g)\ (^4S_{3/2})$ $\Delta H = +75\ 18$
$..3H(g) + P(g) \rightarrow PH_3(g)$ $\Delta H = -3(52\ 1) - 75\ 2 + 2\ 2 = -229\ 3$
P-H bond energy = 229 3/3 = 76 4 kcal /mole

The over-all bond energies, such as the P-H bond energy in phosphine derived above, can be treated as the summation of nonpolar and ionic σ-bond and π-bond parts.

From the valence-bond treatment, we assume that the wave function of the molecule, ψ, can be treated as the sum of orthogonal covalent and ionic functions, viz

$$\psi = \psi_{cov} + \lambda\psi_{ion}$$

From the molecular-orbital treatment, we take the π-orbital concept for multiple bonds This over-all approach is an extension of the one used by Pauling [9] Also see reference 15

The nonpolar σ-bond part is then found to be the sum of contributions from each of the two bonded atoms. The ionic σ-bond part of the over-all energy can also be divided between the two bonded atoms by use of the electronegativity values as defined by Pauling

Thus, in mathematical language, if we let the heat of formation from the spectrographic ground state be equal to ΔH_{sp}, we have the following equation:

$$\Delta H_{sp} = \sum_{all\ bonds} D_{AB} \tag{2-1}$$

where D_{AB} is the over-all bond energy of the bond between atoms A and B.

Likewise,

$$D_{AB} = D_{\sigma, AB} + D_{i, AB} + D_{\pi, AB} \tag{2-2}$$

where D_σ, D_i, and D_π equal the nonpolar σ-bond, the ionic σ-bond, and the π-bond contributions, respectively, to the bond energy

Now we shall assume that the nonpolar σ-bond contribution to the over-all bond energy is an additive function of values which are specific for each bonded atom. Thus,

$$D_{\sigma, AB} = D_{\sigma, A} + D_{\sigma, B} \tag{2-3}$$

where $D_{\sigma, A}$ is a constant for any element, A

[9] L Pauling, *J Phys. Chem*, **56**, 361 (1952)

Electronegativities and σ-Bond Energy Contributions

By one definition of the term "electronegativity," the ionic contribution to the bond energy is proportional to the square of the difference in electronegativity between the two bonded atoms, as shown by the following equation:

$$D_{i,\,AB} = 23.06\,(x_A - x_B)^2 \tag{2-4}$$

If we now confine our interests to those compounds in which it is believed there is little or no multiple bonding, so that D_π must equal zero, thermodynamic data can be used to calculate simultaneously electronegativities and the nonpolar σ-bond contributions to the over-all bond energy. This is done by remembering that the elements, in those allotropic forms in which multiple bonding does not occur, can only contain bonds in which both bonded atoms have the same electronegativity, so that $D_{i,\,A}$ must equal zero. In other words, for the elements in which multiple bonding is not found ($D_{\pi,\,AA} = 0$)

$$D_{AA} = D_{\sigma,\,AA} = 2D_{\sigma,\,A} \tag{2-5}$$

TABLE 2-2
Electronegativities and Nonpolar σ-Bond Energy Contributions

				H
Electronegativity (x)				2 20
Nonpolar σ-bond energy contrib. ($D\sigma$), kcal.				52
	C	N	O	F
Electronegativity (x)	2 60	3 05	3 50	3 90
Nonpolar σ-bond energy contrib. ($D\sigma$), kcal.	32[a]	16	17	18
	Si	P	S	Cl
Electronegativity (x)	1 90	2 15	2 60	3 15
Nonpolar σ-bond energy contrib ($D\sigma$), kcal.	25[b]	25	25	29
	Ge	As	Se	Br
Electronegativity (x)	1 90	2 10	2 55	2 95
Nonpolar σ-bond energy contrib. ($D\sigma$), kcal.	20	19	21	23
	Sn	Sb	Te	I
Electronegativity (x)	1 90	2 05	2 30	2 65
Nonpolar σ-bond energy contrib. ($D\sigma$), kcal	17	17	17	17

[a] Based on ΔH = 137 kcal./mole for Graphite → C(g) ($^3P_0$), instead of the Bureau of Standards value of 171.7

[b] Based on ΔH = 100 kcal /mole for Si(c) → Si(g), instead of the Bureau of Standards value of 88.0.

Then, by working from the elements through the compounds in which multiple bonding is also judged not to occur, a self-consistent set of nonpolar σ-bond energy contributions for the well-known elements which form covalent compounds can be obtained along with a set of electronegativities.

A listing of the most recently calculated[10] nonpolar σ-bond energies and electronegativities is presented in Table 2-2. The electronegativities are given to the nearest 0.05, since it is believed that the values are correct to a precision only slightly less than this. Thus, for hydrogen, the electronegativity of which is reported in the table as 2.20, the mean value obtained from calculations on 13 different compounds is 2.22 ± 0.08; and the value for chlorine obtained on 14 different compounds is 3.12 ± 0.04, which is reported in the table as 3.15. In the case of phosphorus, the nonpolar σ-bond contribution of this element to bond energies is obtained from the following gaseous molecules: PH_3, PCl_3, PBr_3, PI_3, and the P_4 molecule, allowing 3.8 kcal. for the strain energy per bond in the latter molecule. A listing of the phosphorus electronegativities and nonpolar σ-bond energy contributions as computed from these five compounds is given in Table 2-3.

TABLE 2-3
Calculation of Nonpolar σ-Bond Energy Contribution and Electronegativity of Phosphorus

Compound	Experimental bond energy (kcal.)	Calculated electronegativity of P	Calculated bond energy[a] contribution of P (kcal.)
PH_3	76 4	2 20	24 4
PCl_3	78 5	2 12	25 3
PBr_3	63 7	2 12	24 8
PI_3	49[b]	2 10	25
P_4	51 3[c]	—	25 7
	Average	2 14 ± 0 03	25 0 ± 0 5

[a] Based on electronegativity for phosphorus as computed for this compound and the electronegativity and the nonpolar σ-bond energy for the other element from Table 2-1.
[b] Heats of fusion and vaporization were estimated.
[c] Strain energy for "bent bonds" assumed to be 3.8 kcal./bond.

Amount of π-Bonding from Bond Energies

By the use of Table 2-2, the contributions of the nonpolar and the ionic character of the σ-bond to the over-all bond energy can be calculated; but

[10] M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

we are still faced with the problem of estimating the energy corresponding to π-bonding. It is quite probable that a thorough solution to the problem of the π-bond contribution to the over-all bond energy will show that the π-bond contribution is different from element to element, as is now believed to be the case with the nonpolar σ-bond contributions. However, the whole subject of multiple bonding has been sadly neglected for elements other than nitrogen and carbon, and so, for the purposes of this discussion, we will use an average value for the bond energy contribution per π-bond as obtained from selected compounds. From the data given in Table 2-4, it appears that we can make the approximate assumption that the contribution of a single π-bond (either π_y or π_z) is about 50 kcal./mole,[11] assuming that σ-bonds exhibit the same energy regardless of hybridization.

TABLE 2-4
Estimation of the Energy per π-Bond

Compound	Bond	Assumed amount of π-character per σ-bond	Bond energy: Over-all as measured (kcal./mole)	Bond energy: Calculated for σ-bond with ionic contribution (kcal./mole)	Energy per π-bond (kcal./mole)
C_6H_6	C—C	1/2	95	64	62
C_2H_4	C—C	1	107	64	43
C_2H_2	C—C	2	143	64	40
CS_2	C—S	1	109	57	52
HCN	C—N	2	154	53	50
N_2	N—N	2	171	32	70
P_2	P—P	2(?)	117	50	33
				Average	50 ± 10

In Table 2-5 the amount of π-bonding in all the phosphorus compounds for which thermodynamic data are available has been obtained by subtracting from the experimental heat of formation for monatomic gases the heat of formation calculated from the data of Table 2-2 on the assumption that only σ-bonds with ionic character are present. By dividing the difference between the experimental and calculated enthalpies by the number of σ-bonds and then by 50 kcal., an estimate of the number of π-bonds per σ-bond is obtained.[11] As might be expected, the particular diatomic molecules involving phosphorus on which data were available appear to have

[11] J. R. Van Wazer, *J. Am. Chem. Soc.*, **78**, 5709 (1956).

TABLE 2-5
Estimation of π-Bonding from Excess Enthalpy over the Bond Energy Summation

Compound in gaseous state	Heat of formation from monatomic gases: Experimental (kcal /mole)	Heat of formation from monatomic gases: Calculated for σ-bonds with ionic character (kcal./mole)	Excess energy per bond to P (kcal /mole)	Estimated no of π-bonds[a] per σ-bond
Singly connected phosphorus				
P_2	116 6	50	67	1 3
PN	181 0	50	131	2 6
PO	144 1	84	60	1 2
Triply connected phosphorus (primarily-p^3-bonding)				
PH_3	229 3	231	½	0 0
PCl_3	235 1	231	1	0 0
PBr_3	191 2	189	1	0 0
PI_3	147[b]	144	1	0 0
P_2I_4	151[b]	146	1	0 0
P_4	287 7	277[c]	2	0 0
		Average	1	0 0
Quadruply connected phosphorus (primarily sp^3-bonding)				
$POCl_3$	362 9	315	12	0 2
$POBr_3$	315[1]	273	11	0 2
H_3PO_2	480[b]	430	13	0 3
H_3PO_3	625[b]	545	20	0 4
H_3PO_4	757[b]	666	23	0 5
$H_4P_2O_7$	1281[b]	1104	22	0 4
P_4O_{10}	1612 3	1344	17	0 3
		Average	17 ± 4	0 3 ± 0 1
More than four connections (involving d-orbitals)				
PCl_5	305 6	385(331)[d]	−16	0 0
PBr_5	256[b]	315(267)[d]	−12	0 0

[a] Calculated on the assumption that the heat of formation of a π-bond from monatomic gases is 50 kcal /mole

[b] Heats of fusion plus vaporization estimated as follows: PI_3, 16, P_2I_4, 18, $POBr_3$, 14, H_3PO_2, 15; H_3PO_3, 16, H_3PO_4, 18; $H_4P_2O_7$, 30; and PBr_5, 19 kcals

[c] Corrected for strain of 3 8 kcal /bond because of "bent bonds."

[d] Calculated on assumption of four nonpolar σ-bonds and five ionic bond contributions

from one to two π-bonds, *i.e.*, they are multiply bonded. It should be noted here that these diatomic molecules are stable only at elevated temperatures, above 1000°C.

As compared to the diatomic molecules, the molecules in which phosphorus is connected to three neighboring atoms appear to have no multiple bond character. For the molecules in which phosphorus is connected to four other atoms, there appears to be a considerable amount of π-bonding, estimated to be from 0.2–0.5 π-bonds per σ-bond, which figures out as a total lying between one to two π-bonds per phosphorus atom. From this type of calculation, it is impossible to ascribe more or less π-bond character to any particular one of the four bonds coming from each phosphorus atom.

In the case of PCl_5 and PBr_5, there is no evidence for π-bonding from the simple thermodynamic calculation; and, indeed, it appears that there are less than five σ-bonds in these molecules. To a rough approximation, the observed heats of formation can be explained by saying that there is resonance between four σ-bonds with the expected amount of ionic character and one bond which has only ionic character The problem of bonding in those compounds in which phosphorus exhibits the geometry of an sp^3d-hybrid has recently been studied[12] from a quantum mechanical viewpoint.

BOND LENGTHS

The distance between the centers of the electron clouds of two atoms in a molecule is defined as a bond length. It appears that this bond length can be considered to be made up of a nonpolar σ-bond distance from which may be subtracted bond shortenings due to the ionic character and π-contributions to the over-all bond. Considerable evidence shows that the nonpolar σ-bond lengths can be considered as the sum of the so-called σ-bond or single bond radii of the two atoms bonded together. Furthermore, it is assumed that single bond radii are independent of the type of hybridization. Thus,

$$\text{Nonpolar } \sigma\text{-bond length} = r_A + r_B \tag{2-6}$$

for the bond between atoms A and B. Two approaches have been reported in the literature for determining the shortening due to ionic character. One of them introduced by Schomaker and Stevenson[13] is an empirical correction in which the electronegativity difference of the bonded atoms is multiplied by 0.09.

$$\text{Ionic shortening of } A\text{—}B \text{ bond} = 0.09\,|x_A - x_B| \tag{2-7}$$

[12] D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, **1956**, 4895.

[13] V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

TABLE 2-6
Nonpolar σ-Bond and Constant Energy Radii[a] of Certain Atoms in A.

Atom	H	H	H	H
In bonds with elements of	1st row	2nd row	3rd row	4th row
Nonpolar σ-bond				
Huggins	0 36	0 34	0 33	0 32
Schomaker and Stevenson	0 37	0 37	0 37	0 37
Constant energy				
Huggins	0 86	0 84	0 83	0 82
Atom	C	N	O	F
Nonpolar σ-bond				
Huggins	0 77	0 75	0 74	0 72
Schomaker and Stevenson	0 77	0 74	0 74	0 72
Constant energy				
Huggins	1 22	1 12	1 12	1 11
Atom	Si	P	S	Cl
Nonpolar σ-bond				
Huggins	1 15	1 11	1 04	1 00
Schomaker and Stevenson	1 17	1 10	1 04	0 99
Constant energy				
Huggins	1 57	1 53	1 46	1 44
Atom	Ge	As	Se	Br
Nonpolar σ-bond				
Huggins	1 21	1 24	1 17	1 14
Schomaker and Stevenson	1 22	1 21	1 17	1 14
Constant energy				
Huggins	1 61	1 63	1 58	1 56
Atom	Sn	Sb	Te	I
Nonpolar σ-bond				
Huggins	1 42	1 45	1 41	1 35
Schomaker and Stevenson	1 40	1 41	1 37	1 33
Constant energy				
Huggins	1 80	1 83	1 79	1 73

[a] The Huggins nonpolar radii are to be used in equation 2-8, the Schomaker-Stevenson radii in equation 2-7, and the Huggins constant energy radii in equation 2-9.

The question may be raised as to whether the Stevenson-Schomaker correction includes recognition of shortening due to π-bonding, which, of course, it should not. Pauling concludes that this correction does not include π-bonding since it gives a correct measure of the shortening in the

C—N and C—O bonds of trimethylamine and dimethyl ether. According to Pauling, no π-bonding is to be expected for either of these compounds, because the carbon, which is the more electropositive atom in either the C—N or C—O bond, is given a negative charge by the partial ionic character of its bonds to hydrogen. This means that the carbon should not have a free π-orbital to accept electrons from the nitrogen or oxygen atoms.

According to Huggins,[14] the shortening due to ionic character in σ-bonds should be equal to half the logarithm of the quantity obtained by dividing the nonpolar σ-bond energy plus the ionic contribution to the bond energy by the σ-bond energy without ionic contributions, the factor $^1/_2$ being obtained in a rather arbitrary manner

$$\text{Ionic shortening of } A\text{—}B \text{ bond} = {}^1/_2 \log (D_{\sigma,\,AB} + D_{i,\,AB})/D_{\sigma,\,AB} \quad (2\text{-}8)$$

The sets of covalent radii reported by Huggins and by Schomaker and Stevenson are given in Table 2-6. As exemplified by Table 2-7, use of the Schomaker-Stevenson radii with the Schomaker-Stevenson correction for ionic shortening gives about the same answer as use of the Huggins radii and correction for ionic shortening. Another set of radii, r^*, called the constant energy radii, have also been presented by Huggins.[14] According to the theory behind these radii, departures from additivity for atomic radii in the absence of π-bonding are due to variations in the bond energy. The constant energy radii are used with the following equation for calculating atom-center distances. Either experimental bond energies can be employed (in which case a partial correction for π-bond shortening is introduced if there is some multiple bonding) or values can be taken from Table 2-2 or Appendix B. It should be noted that the bond energy term in equation 2-9, $^1/_2 \log (D_{\sigma,\,AB} + D_{i,\,AB})$, is much larger than the ionic corrections given in equations 2-7 and 2-8.

$$\text{Correct } \sigma\text{-bond length} = r_A^* + r_B^* - {}^1/_2 \log (D_{\sigma,\,AB} + D_{i,\,AB}) \quad (2\text{-}9)$$

π-Bond Shortening

The question of bond shortening due to multiple bond formation has been covered in a recent publication by Pauling.[15] In accord with this article, a potential function for the bond has been calculated on the basis that the force constants of single, double, and triple bonds are in the ratio of 1:3:6 and that the shortening due to π_y alone is equal to 0.19 A. and for $\pi_y + \pi_z$ is equal to 0.30 A. The curve resulting from this calculation is shown in

[14] M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4126 (1953).

[15] L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

Figure 2-4, in which it should be noted that greater shortening and hence a minimum free energy for the bond is obtained when the π_y and π_z contributions are always of equal amount. When the π_y character of the bond is increased to unity before there is a contribution from π_z, the curve exhibits a cusp, and the bond has a higher free energy. In the everyday language of chemistry, this means that a more stable configuration is achieved by pure triple bond character than by an electronically equivalent amount of double bond character

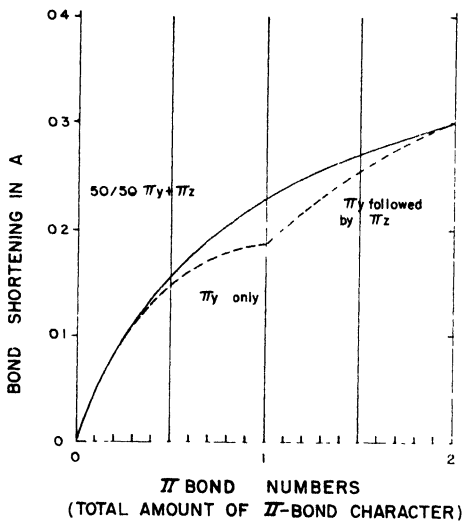


Fig 2-4 Calculated shortening in internuclear distances between atoms due to π-bonding

In Table 2-7, the amount of π-bonding in the various types of phosphorus compounds is computed from the bond distances The computations given in this table have been made in two ways. According to one, the nonpolar σ-bond radii given by Schomaker and Stevenson were employed with their empirical correction for ionic character of the bond. In the other, the Huggins nonpolar σ-bond radii were used with his ionic-character correction based on bond-energy data. In all but a few exceptional cases, the calculated bond distances were equal to or longer than the experimentally observed distances, and any difference between calculation and experiment was attributed to π-bond shortening. By employing Figure 2-4, an estimate was made of the amount of π-bonding per σ-bond.

TABLE 2-7
Amount of Multiple Bonding in Various Phosphorus Compounds[a]

Compound	Bond	Observed atom-center distance (A)	Calculated number of π-bonds/σ-bond		π-Bonds per P atom	
			S and S	H	S and S	H
Singly connected phosphorus						
P_2	P—P	1 890	2 2	2 4	ca. 2	ca. 2
PN	P—N	1 491	1 7	1 7	ca. 2	ca. 2
PO	P—O	1 447	1 3	1 1	ca. 1	ca. 1
PC	P—C	1 5622	1 7	2 2	ca 2	ca. 2
PH	P—H	1 429	0 0	0 0	0 0	0 0
Triply connected phosphorus (primarily p^3-bonding)						
PH_3	P—H	1 424 ± 0 005	0 1	0 0	0 3	0 0
PF_3	P—F	1 546 ± 0 008	0 2	0 1	0 6	0 3
$PFCl_2$	P—F	1 55 ± 0 03	0 2	0 1	0 2	0 1
	P—Cl	2 02 ± 0 02	0 0	0 0		
PCl_3	P—Cl	2 00 ± 0 02	0 0	0 1	0 0	0 0–0 3
		2 03 ± 0 02	—	0 0		
PBr_3	P—Br	2 23 ± 0 01	—	—	0 0	0 0
PI_3	P—I	2 52 ± 0 01	—	—	0 0	0 0
		2 43 ± 0 04	—	0 0		
P_4O_6	P—O	1 67 ± 0 03	0 1	0 0	0 3	0 2
		1 65 ± 0 02	0 1	0 1		
$P(CH_3)_3$	P—C	1 87 ± 0 02	0 1	0 0	0 3	0 0
Cryst. P_4	P—P	2 205	0 0	0 0	0 0	0 0
P_4 liquid	P—P	2 25 ± 0 08	—	—	0 0	0 0
Amorph. red P	P—P	2 29 ± 0 08	—	—	0 0	0 0
Cryst. black P	P—P	2 18 ± 0 02	0 0	0 0	0 0	0 0
Amorph. black P	P—P	2 27 ± 0 03	—	—	0 0	0 0
P_4S_3	P—P	2 24 ± 0 03	—	—	0 0	0 0
	P—S	2 17 ± 0 02	—	—		
P_4S_7	P—P	2 35 ± 0 01	—	—	0 0	0 0
	P—S	2 08 ± 0 01	0 0	0 1	0 0	0 2

P_4S_5	P—S in PS_3	2 14 ± 0 03	—	—	0 0	0 0
	P—S in P_3S ring	2 19 ± 0 03	—	—		
	P—S from P in P_3S ring	2 09 ± 0 03	0 0	0 1		
	P—P in P_3S ring	2 21 ± 0 03	0 0	0 0		
				Average	0 1 ± 0 1	0 1 ± 0 1
Quadruply connected phosphorus (primarily sp^3-bonding)						
PH_4^+ in PH_4Cl	P—H	1 42 ± 0 02	0 1	0 0	0 4	0 0
PO_4^{3-} in H_3PO_4	P—O	1 57 ± 0 02	0 3	0 3	1 5	1 4
	P—O	1 52 ± 0 02	0 6	0 5		
PO_4^{3-} in KH_2PO_4	P—O	1 56 ± 0 01	0 4	0 3	1 6	1 2
		1 53–1 58 ± 0 01	0 3–0 5	0 2–0 4	1 6	1 2
PO_4^{3-} in $NH_4H_2PO_4$	P—O	1 50 ± 0 01	0 7	0 6	2 8	2 4
		1 49–1 59 ± 0 01	0 3–0 7	0 2–0 6	2 0	1 6
PO_4^{3-} in $\beta Ca_3(PO_4)_2$	P—O	1 56 ± 0 02	0 4	0 3	1 6	1 2
PO_4^{3-} in BPO_4	P—O in P—O—B	1 55 ± 0 02	0 4	0 3	1 6	1 2
PO_4^{3-} in $AgPO_4$	P—O in P—O—Ag	1 61 ± 0 03	0 2	0 2	0 8	0 8
PO_4^- in Φ_2HPO_4	P—O in P—O—Φ	1 55 ± 0 02	0 4	0 3	2 1	1 6
	P—O in P—O—H	1 55 ± 0 02	0 4	0 3		
	P—O isolated	1 47 ± 0 02	0 9	0 7		
OPO_4^{2-} in ZrP_2O_7	P—O in P—O—P	1 56 ± 0 04	0 4	0 3	1 6	1 2
	P—O isolated	1 52 ± 0 04	0 6	0 5		
$OP(O)_2$–O in $(NH_4)_4P_4O_{12}$	P—O in P—O—P	1 59–1 63 ± 0 01	0 2–0 3	0 1–0 2	2 1	1 8
	P—O isolated	1 44–1 51 ± 0 01	0 6–1 0	0 5–1 0		
$OP(O)_2$–O in $(RbPO_3)_n$	P—O in P—O—P	1 62 ± 0 03	0 2	0 1	2 4	1 8
	P—O isolated	1 46 ± 0 03	1 0	0 8		
P_4O_{10}	P—O in P—O—P	1 62 ± 0 02	0 2	0 1	2 5	1 7
	P—O isolated	1 39 ± 0 02	1 9	1 4		
$P_4O_6S_4$	P—O	1 61 ± 0 02	0 2	0 2	1 6	1 7
	P—S	1 85 ± 0 02	1 0	1 1		
P_4S_{10}	P—S in P—S—P	2 09 ± 0 03	0 0	0 1	0 3	0 7
	P—S isolated	1 96 ± 0 03	0 3	0 4		
P_4S_7	P—S in P—S—P	2 07 ± 0 02	0 1	0 1	0 7	0 8
	P—S isolated	1 95 ± 0 02	0 4	0 5		

(continued)

TABLE 2-7 (*continued*)

Compound	Bond	Observed atom-center distance (A)	Calculated number of π-bonds σ-bond		π-Bonds per P atom	
			S and S	H	S and S	H
P_4S_5	P—S in P—S—P	2 09 ± 0 03	0.0	0 0	0 4	0 5
	P—S isolated	1 94 ± 0 03	0 4	0 5		
	P—P	2 21 ± 0 03	0 0	0 0		
HPO_3^{2-} in $MgHPO_3$	P—O	1 51 ± 0 03	0 6	0 5	1 8	1 5
$(H_3N^+PO_3^-)^-$	P—O	1 51 ± 0 02	0 6	0 5	1 8	1 5
	P—N	1 78 ± 0 02	—	—		
$(PNCl_2)_4$	P—N	1 65 ± 0 04	0 2	0 2	0 6	0 6
	P—Cl	1 97 ± 0 03	0 1	0 1		
$(PNCl_2)_4$	P—N	1 67 ± 0 03	0 2	0 2	0 4	0 6
	P—Cl	1 99 ± 0 03	0 0	0 1		
POF_3	P—O	1 56 ± 0 03	0 4	0 3	1 9-1 3	1 5-0 9
		1 45 ± 0 03	1 0	0 9		
	P—F	1 52 ± 0 02	0 3	0 2		
POF_2Cl	P—O	1 55 ± 0 03	0 4	0 3	1 0	0 7
	P—F	1 51 ± 0 03	0 3	0 2		
	P—Cl	2 01 ± 0 04	0 0	0 0		
$POFCl_2$	P—O	1 54 ± 0 03	0 5	0 4	0 9	0 8
	P—F	1 50 ± 0 03	0 4	0 2		
	P—Cl	1 99 ± 0 04	0 0	0 1		
$POCl_3$	P—O	1 45 ± 0 05	1 0	0 9	1 0	1 2
	P—Cl	1 99 ± 0 02	0 0	0 1		
$POBr_3$	P—O	1 44 ± 0 10	1 1	1 0	2 0	1 9
	P—Br	2 06 ± 0 03	0 3	0 3		
PSF_3	P—S	1 85 ± 0 02	1 0	1 1	1 9	1 7
		1 87 ± 0 02	0 8	1 0		
	P—F	1 51 ± 0 02	0 3	0 2		
		1 53 ± 0 02	0 3	0 2		

$PSCl_3$	P–S	1 94 ± 0 03	0 4	0 5	1 0–0 4	1 1–0 5
		1 85 ± 0 02	1 0	1 1		
	P–Cl	2 01 ± 0 02	0 0	0 0		
		2 02 ± 0 02	0 0	0 0		
PSF_2Br	P—S	1 87 ± 0 05	0 8	1 0	2 1	1 9
	P—F	1 45 ± 0 08	0 6	0 4		
	P–Br	2 14 ± 0 04	0 1	0 1		
$PSFBr_2$	P—S	1 87 ± 0 05	0 8	1 0	1 2	1 2
	P—F	1 50 ± 0 10	0 4	0 2		
	P—Br	2 18 ± 0 03	0 0	0 0		
$PSBr_3$	P—S	1 89 ± 0 06	0 7	0 8	1 0	1 1
	P—Br	2 13 ± 0 03	0 1	0 1		
$(PCl_4)^+$ in PCl_5	P—Cl	1 98 ± 0 01	0 0	0 1	0 0	0 4
$(PCl_4)^+$ in PCl_6I	P—Cl	1 98 ± 0 02	0 0	0 1	0 0	0 4
				Average	1 2 ± 0 5	1 0 ± 0 5
More than four connections (involving d-orbitals)						
PF_5	P–F	1 57 ± 0 02	0 2	0 1	0 8	0 3
	P–F apical	1 59 ± 0 03	0 1	0 0		
PF_3Cl_2	P—F	1 59 ± 0 03	0 1	0 0	0 3	0 0
	P—Cl	2 05 ± 0 03	0 0	0 0		
PCl_5	P—Cl	2 01 ± 0 05	0 0	0 0	0 0	0 0
	P—Cl apical	2 07 ± 0 05	—	—		
$(PCl_6)^-$	P—Cl	2 04 ± 0 02	0 0	0 0		
	P—Cl apical	2 08 ± 0 01	—	—	0 0	0 0
PF_6^-	P—F	1 58 ± 0 02	0 1	0 1	0 4	0 4
	P—F apical	1 73 ± 0 02	—	—		
				Average	0 3 ± 0 1	0 1 ± 0 1

[a] Theoretical σ-bond distances corrected for ionic shortening are taken from Appendix B.

As might be expected, the diatomic molecules P_2, PN, and PC showed a large amount of π-bonding, practically equivalent to a triple bond connecting the presence of only one electron in the hydrogen atom; and the PO molecule appears to have a double bond. All of these diatomic molecules are unstable at room temperature, and data concerning them were obtained from spectrographic measurements.

For the compounds in which the phosphorus is connected to three neighboring atoms, the amount of π-bonding was generally found to be very small (zero, within experimental error, for most cases). But, for the compounds in which the phosphorus is connected to four other atoms, the amount of π-bonding was generally high. In the case of the compounds in which the phosphorus is connected to more than four other atoms, the amount of π-bonding was again very small, and the largest number of negative values for the shortening were observed here. Presumably, the negative values for the shortening indicate that these compounds do not even exhibit a complete σ-bond between the phosphorus atom and its neighbors.

In view of the rough approximations and insufficiently accurate data which were employed, the relatively good agreement between the amount of π-bonding estimated from the atom-center distances in Table 2-7 and from the enthalpy data in Table 2-5 is most gratifying. This good agreement does not, however, show that π-bonding is the common cause for the observed bond shortenings and excess enthalpies—rather, it merely demonstrates that energy values are closely related to atom-center distances, as would be expected. Justification for attributing the observed effects to π-bonding comes from recent quantum mechanical calculations[16] in which it is shown that π-bonds involving a *d*-orbital of one atom and a *p*-orbital of another should be both common and important and that the strength of such bonds ought to be relatively independent of the difference in electronegativity between the bonded atoms.

From the available experimental information, several generalities can be made concerning the phosphorus compounds which are stable under normal conditions: (1) In those compounds in which phosphorus shares electrons with three neighboring atoms, there are three σ-bonds, with little or no π-character, from the phosphorus. (2) In those compounds in which phosphorus shares electrons with four neighboring atoms, there are four σ-bonds, with an average of about one π-bond per phosphorus atom. (3)

[16] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332; H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954); *J. Chem. Phys.*, **21**, 258 (1953). Also see E. R. Lippincott and R. Schroeder, *J. Am. Chem. Soc.*, **78**, 5171 (1956).

When electrons are shared with five or six neighboring atoms, there is less than one full σ-bond for each connection between the phosphorus and a neighboring atom with apparently very little π-bonding.

These generalities are in accord with quantum mechanical reasoning[17] which shows that π-bonding should generally be found in structures based on quadruply connected phosphorus, whereas, for the triply connected phosphorus and phosphorus having more than four attached atoms, π-bonding appears in relatively small amounts only for highly electronegative ligands. Thus, fluorine, in Table 2-7, is seen to contribute nearly as much shortening (assuming the tabulated values for the fluorine bond radius are correct) to the P—F bond in the triply connected as in the quadruply connected phosphorus compounds. On the other hand, chlorine appears to exhibit essentially no shortening in any of the structures reported in Table 2-7. Except for the diatomic molecules, all of the π-bonding discussed in Table 2-7 is attributable to the *d*-electrons of the phosphorus. In the diatomic molecules, however, phosphorus has *p*-orbitals available; and, in these compounds, we undoubtedly deal with simple π-bonds based exclusively, or almost exclusively, on p_π-orbitals

It is interesting to note that π-bonds around a quadruply connected phosphorus atom do not couple[18] very much with the π-bonds of phenyl groups. This conclusion is based on the ultraviolet absorption spectra of the benzene rings in $C_6H_5PO_3H_2$, $C_6H_5(H)PO_2H$, $C_6H_5(R)PO_2H$, $(C_6H_5)_2PO_2H$, $(C_6H_5)_3P$, and $(C_6H_5)_3PO$. These spectra show that the phenyl groups are only weakly conjugated with the quadruply connected phosphorus, and that there is no detectable resonance between several phenyl groups attached to the same quadruply connected phosphorus atom. However, for triply connected phosphorus (or other atoms exhibiting unshared electron pairs) extensive conjugation between benzene rings attached to a given central atom is found. The existence of π-bonding in sp^3 σ-bond base hybrids of the second row elements appears to be quite general[15]—as shown by a recent review[19] giving experimental evidence for d_π-orbitals in silicon.

STRUCTURES FROM NUCLEAR MAGNETIC RESONANCE

As previously mentioned in Chapter 1, measurement of the nuclear magnetic resonance of phosphorus in its compounds offers an interesting new

[17] H. H. Jaffé, *J. Inorg. Nuclear Chem.*, **4**, 372 (1957).

[18] H. H. Jaffé, *J. Chem. Phys.*, **22**, 1430 (1954); H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069, 2930 (1952)

[19] F. G. A. Stone and D. Seyferth, *J. Inorg. Nuclear Chem.*, **1**, 112 (1955).

technique[20] for obtaining information concerning the variation in the electron distribution about the phosphorus atom from compound to compound and hence about the type of bonding. For a given nucleus—such as phosphorus—exhibiting a magnetic moment, the resonance frequency is proportional to the magnetic field at the nucleus This field is affected by the extranuclear electrons of the atom so that, at resonance, a change in the electronic environment which reduces the magnetic field at the nucleus will obviously necessitate an increase in the applied magnetic field to maintain resonance. Such an increase is called a positive chemical shift. These shifts, which may be either positive or negative, are measured in parts per million (p.p.m.) of the applied magnetic field relative to a chemical compound of the element in question which is arbitrarily chosen as a reference. The usual reference[21] for phosphorus is 85% orthophosphoric acid at 25°C. The chemical shifts in parts per million are thus defined as $(H_r - H_\tau)\text{-}10^6/H_\tau$ where H_r and H_τ are the magnetic fields for the sample under study and the 85% orthophosphoric acid reference, respectively, at the resonance point using a fixed radio frequency. When measured in parts per million, chemical shifts are invariant to the resonance frequency, being the same whether a low frequency is used at a low applied magnetic field or a high frequency is used at a high applied magnetic field

The type of nuclear magnetic resonance study which is described here is usually called "high resolution" spectroscopy, as opposed to low resolution work by means of which crystal geometries are investigated or the magnetic nuclei in a mixture of isotopes of various elements are determined. The term "high resolution" is employed because the chemical shifts are small and hence must be measured with precision. Since the dipole-dipole coupling between molecules in solids causes considerable broadening of the nuclear magnetic resonance spectra of solids, and since the nuclear resonance in solids is thereby coupled to the thermal vibrations of the crystal lattice,[20] high resolution measurements must usually be carried out on liquid samples (melts, solutions, etc.) placed in extremely homogeneous magnetic fields An important aspect of high resolution nuclear magnetic resonance spectra is that the area under a peak or set of peaks correspond-

[20] H. S. Gutowsky *et al.*, *Discussions Faraday Soc.*, **19**, 187–246 (1955); J. E. Wertz, Nuclear and Electronic Spin Magnetic Resonance, *U. S. Air Force Report* OSR-TN-55-203 [not classified and issued under Contract AF 18(600)-479] May, 1955; E. R. Andrews, *Nuclear Magnetic Resonance*, University Press, Cambridge, England, 1955

[21] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956). N. Muller, P. C. Lauterbur, and J. Goldenson, *ibid.*, **78**, 3557 (1956). H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954)

ing to a given kind of nucleus is proportional to the amount of that nucleus present in the sample, when the measurement is carried out under normal conditions

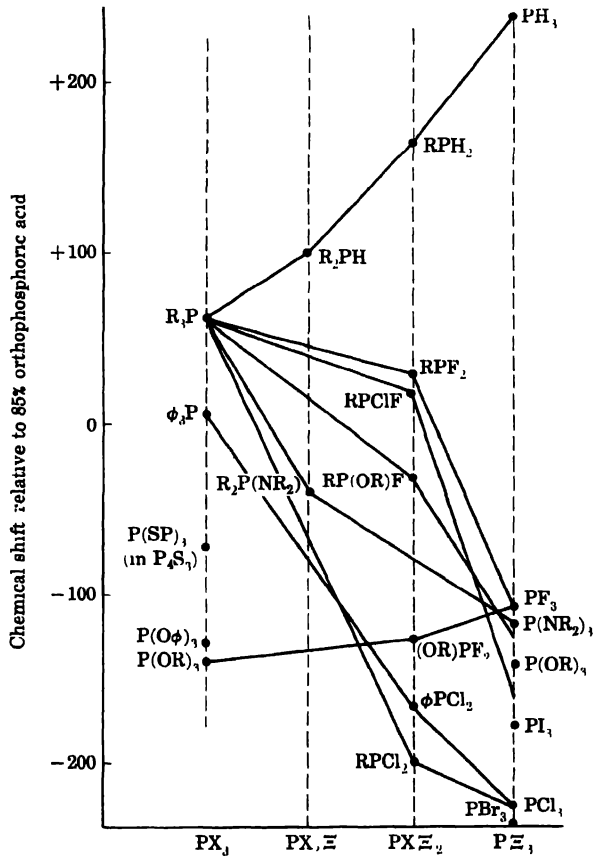
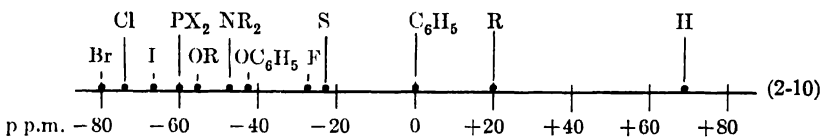


Fig 2-5 Chemical shifts from the nuclear magnetic resonance of triply connected phosphorus compounds.

Data on high resolution $_{15}P^{31}$ nuclear magnetic resonance of several hundred phosphorus compounds have been presented by Van Wazer *et al.*[21] Several general observations can be made immediately upon inspection of the data. First, very large chemical shifts are found for the triply connected phosphorus atoms. These shifts cover a range of about 500 p.p.m. as compared to a range of 100 p.p.m. (with the majority within 50 p.p.m.) for the quadruply

connected phosphorus atoms studied. Secondly, large positive shifts with respect to the quadruply connected phosphorus are found for phosphorus atoms connected to more than four other atoms. And, thirdly, bent bonds in a compound also appear to make rather large positive shift contributions.

In Figure 2-5 chemical shifts for a number of compounds based on triply connected phosphorus are plotted in terms of families in which the X atoms in PX_3 are substituted consecutively by Ξ atoms, so that the range of compounds between PX_3 and $P\Xi_3$ are covered. It is apparent from this figure that the various ligands attached to a triply connected phosphorus atom make a roughly constant contribution to the over-all shift, no matter what reference point is chosen from which to measure the shift. By using orthophosphoric acid as the reference, these roughly constant resonance shift-contributions for the various substituent atoms or radicals are



By adding the appropriate shift contributions, the chemical shift of any triply connected phosphorus atom can be approximated—in many cases to about ±(10–20) p.p.m. An exceptionally inaccurate case is found in RPClF, for which a shift of −85 p.p.m. is calculated from the shift contribution of equation 2-10, as compared to the measured shift of +20 p.p.m. Although the basic theory of nuclear magnetic resonance is quite well developed,[20,22] it has been applied[23] only in a semiempirical manner to the computation of chemical shifts of triply connected phosphorus, while the detailed explanation of the chemical shifts in quadruply connected phosphorus is still lacking. It appears that the chemical shift is primarily dependent on the 3*p*-electrons of the phosphorus atom with 3*s*-electrons making essentially no contribution and the electrons in the closed subvalence shells also having little effect. The chemical shift, δ, is related to D, the number of unbalanced *p*-electrons in the valence shell of the triply connected phosphorus, by the following equation:

$$\delta = -230 + 29.0 \times 10^3 e^{-46.0\,D} \qquad (2\text{-}11)$$

[22] N. F. Ramsey, *Phys Rev.*, **77**, 567 (1950); *ibid.*, **78**, 699 (1950); *ibid.*, **86**, 243 (1952).

[23] J. R. Parks, *J. Am. Chem. Soc*, **79**, 757 (1957). Also see ref. 21 and A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

The factor D in this equation is related to the electronegativity, x, of the attached atoms and the bond angle, θ, by the following equation which applies to those triply connected phosphorus compounds in which all three atoms attached to the phosphorus are alike.

$$D = (3/4 - \beta^2)\beta^2(1 - \epsilon)$$

where $\beta = -3\cos\theta/(1 - \cos\theta)$, and

$$|\epsilon| = 0.16|x_P - x_A| + 0\,035|x_P - x_A|^2 \qquad (2\text{-}12)$$

The fact that bond angles in compounds based on triply connected phosphorus are determined, at least to a first approximation, by the electronegativity differences of the attached atoms leads to the fact that various substituent groups exhibit approximately fixed contributions to the over-all chemical shift. According to the approximate theory given here, the wave function asymmetry of the phosphorus atom is zero for both p^3- and pure sp^3-hybrids, so that the asymmetry becomes a maximum for the intermediate bond angle of 98°. This agrees with the finding that the shift contributions of various substituent atoms shows a minimum value at an intermediate electronegativity of about 2.8. This means that shielding of the phosphorus decreases with increasing electronegativity of substituent atoms having electronegativities lower than about 2.8, with the reverse being true for substituent atoms having higher electronegativities.

In compounds based on quadruply connected phosphorus, each substituent atom or radical again, to a first approximation, appears to make a given contribution to the over-all chemical shift. This effect is shown by the data of Table 2-8, in which the shifts due to the substitution of oxygen by other atoms are reported. It should be noticed that replacement of oxygen by any of the elements listed (H, C, N, P, S, Cl, and Se) leads to a negative shift, except for fluorine, which gives a positive shift. This means that replacement of oxygen by less electronegative elements gives less shielding and *vice versa*. From the data of Table 2-8 shielding of quadruply connected phosphorus by substituent elements is seen to lie in the order: $Sc < S < C_{aliphatic} < C_{aromatic} \approx P < N \approx Cl < H < O < F$—which, with the exception of hydrogen and phosphorus, is the order of increasing electronegativity.

Comparison of the shifts found by substituting nitrogen for oxygen to those found by substituting sulfur for oxygen is of interest because these three elements are close to each other in the periodic table and because there are considerable data available. Although a wide variety of structures were employed in either case, the oxygen-to-nitrogen shift is quite

TABLE 2-8
Chemical Shifts for Quadruply Connected Phosphorus on Which Oxygen Is Replaced by Another Substituent Atom

No	Element replacing oxygen	Original structure	Replaced structure	Total shift due to replacement (p p m.)	Shift per replaced atom (p p m)
1	H	$C_6H_5PO(OH)_2$	$C_6H_5P(O)H(OH)$	− 4	− 4
2		$HOPO_3^{2-}$	$HOPH(O)_2^-$	− 4	− 4
3		$HOPO_3^{2}$	$HOPH_2(O)$	−13	− 7
4		PO_4^{2-}	$H_2PO_2^-$	− 3	− 2
5		$(RO)_2PO_2^-$	$(RO)_2PH(O)$	− 8	− 8
6	C aliphatic	PO_4^{3-}	RPO_3^{2-}	−22	−22
7		$HOPO_3^{2-}$	$RPO_2(OH)^-$	−32	−32
8		$(R_2N)_3PO$	$(R_2N)_3PR^+$	−37	−37
9	C aromatic	$C_6H_5SPO(OR)_2$	$C_6H_5SPC_6H_5(O)(OR)$	−17	−17
10		$HOPH(O)_2^-$	$C_6H_5PH(O)_2^-$	−18	−18
11		$HOPO_3^{2-}$	$HOPC_6H_5(O)_2^-$	−16	−16
12		$(RO)_2PO_2^-$	$(RO)_2PC_6H_5(O)$	−19	−19
13		$ROPO_3^{2-}$	$ROP(C_6H_5)_3(O)$	−27	−14
14		PO_4^{3-}	$(C_6H_5)_3PO$	−18	− 6
15		$(R_2N)_3PO$	$(R_2N)_3PC_6H_5^+$	(−23)	(−23)
16	N	$(HO)_2PO_2$	$(HO)P(NH_2)(O)_2$	− 3	− 3
17		$(C_6H_5O)_2P(OR)(O)$	$(C_6H_5O)_2P(NHR)(O)$	−13	−13
18		$\rangle POP(O)_2^-OP\langle^-$	$\rangle PNP(O)_2NP\langle^-$	−19	−10
19		$(RO)_3PO$	$(RO)P(NR_2)_2(O)$	−21	−11
20		$(RO)_2P(O)OP(O)(OR)_2$	$(R_2N)_2P(O)OP(O)(NR_2)_2$	−21	−11

21		$(RO)_3PO$	$(R_2N)_3PO$	−27	− 9
22		$RP(O)(OR)_2$	$RP(NR_2)_3^+$	−31	−10
23		$(X_3C)P(O)(OR)_2$	$(X_3C)P(NR_2)_3^-$	−37	−12
24		$RC_6H_5CH_2P(O)(OH)_2$	$(ClC_6H_5CH_2P(NR_2)_3^-$[a]	−30	−10
25	F	$RO(PO_3)^{2-}$	$RO(PF_2(O)$	+20	+10
26	P	$(HO)_2(O)PO(P(O)(OH)_2$	$(HO)_2(O)PP(O)(OH)_2$	−19	−19
27	S	$(RO)_2PO(OC_6H_5)$	$(RO)_2PO(SC_6H_5)$	−26	−26
28		$C_6H_5P(O)(OR)(OC_6H_5)$	$C_6H_5P(O)(OR)(SC_6H_5)$	−25	−25
29		$(RO)_3PO$	$(RO)_2P(SR)(O)$	−33	−33
30		$C_6H_5PO(Cl)_2$	$C_6H_5PS(Cl)_2$	−46	−46
31		Cl_3PO	Cl_3PS	−28	−28
32		$(RO)_2PO_2^-$	$(RO)_2P(S)_2^-$	−57	−57
33		$(C_6H_5O)_3PO$	$(C_6H_5O)_3PS$	−71	−71
34		$(RO)_2PO(OC_6H_5)$	$(RO)_2PS(OC_6H_5)$	−46	−46
35	Cl	$>PNP(O)_2-NP<$	$>PNP(Cl)_2NP<$	−20	−10
36		$(RO)PO_3^{2-}$	$(RO)PCl_2(O)$	− 6	− 3
37		$ClCH_2PO(OR)_2$	$ClCH_2PO(Cl)_2$	−18	− 9
38		$C_6H_5PO_2(OH)$	$C_6H_5PO(Cl)_2$	−16	− 8
39		PO_4^{2-}	$OPCl_3$	0	0
40	Se	$(RO)_3PO$	$(RO)_3PSe$	−73	−73

[a] A change of substituent in the *para*-position should affect the shift by no more than a few p p m

consistent at -11 ± 2 p.p.m. per atom (except for item 16 in Table 2-8); whereas, the oxygen-to-sulfur shift varies from -25 to -71 p.p.m. per atom. This means that in most structures the nitrogen substitutes for oxygen in the same way each time, whereas there is a variable change in bonding type when sulfur substitutes for oxygen. Inspection of the data indicates that the sulfur-for-oxygen shift is -25 to -30 p.p.m. for bridging positions (*e.g.*, C-S-P for C-O-P), and it is about -60 p.p.m. for the isolated position. In view of the differences between the amount of π-character in P—O and in P—S bonds, as well as the effect in which π-bonding is concentrated in connections to isolated (nonbridging) atoms, such a difference between isolated and bridging positions is not surprising.

Although the theory of nuclear magnetic resonance has not yet been expressed in the form of a usable equation applicable to compounds based on quadruply connected phosphorus, it would seem that the chemical shifts found for such phosphorus atoms are probably due in a significant part to changes in the distribution of π-bonds among the four σ-bonds. The observed action of substituents exhibiting relatively low electronegativities in reducing the magnetic shielding of the phosphorus nucleus is thus explained by the action of these ligands in shifting π-bonds within the σ-bonded sp^3-hybrid structure so as to upset the electronic symmetry of the system. It should be noted that the shift contributions of the various ligands are unaffected by ionization of the phosphorus-containing moiety; *i.e.*, to a first order the same phosphorus spectrum is found for a given group whether present in an anion, cation, or neutral molecule, and the counter ions have no effect.

Since there are not sufficient nuclear magnetic resonance data on compounds in which phosphorus is connected to more than four neighboring atoms, no general remarks will be made here on chemical shifts for these compounds.

In addition to chemical shift data, a great deal of information can be obtained about the structures of molecules and molecule-ions from the phenomenon called indirect spin-spin splitting.[24] This phenomenon is an indirect coupling of two or more magnetic nuclei in the same molecular structure by a mechanism which can be qualitatively described[20] as follows: Consider two nuclei, A and B, both exhibiting magnetic spin. When an electron is in the vicinity of nucleus A, it becomes polarized by the local magnetic field of A. Thus, when this polarized electron travels over to nucleus B, it changes the magnetic field at that nucleus. In different mole-

[24] H. S. Gutowsky and D. W McCall, *J. Chem. Phys.*, **21**, 279 (1953).

cules, A will have different orientations with respect to the main magnetic field, so that in the bulk sample, the resonance peak due to the B nuclei is split into a number of components given by the possible orientations of the A nuclei, with the intensities of the component peaks depending on the statistical weights of the orientations of A. This indirect interaction is a mutual coupling phenomenon, so that the resonance peaks of both atoms A and B are split by equal amounts in terms of energy. This splitting, when measured in cycles per second, is independent of applied magnetic field, whereas it is dependent if expressed in terms of parts per million. This means that in a sample giving a complicated spectrum, chemical shifts and spin-spin multiplets can often be unscrambled by observing the over-all resonance pattern at different applied magnetic fields. Another method for demonstrating spin-spin splitting is to apply a radio-frequency electric field at the resonance frequency of the atom doing the splitting (*e.g.*, H in PH_3), while recording the resonance pattern of the atom being split (*e.g.*, P in PH_3). Under these conditions the multiplet structure due to spin-spin coupling vanishes.

Since a nuclear electric quadrupole moment affords a relaxation mechanism which obliterates the multiplet structure due to indirect spin-spin coupling, observable multiplets in nuclear magnetic resonance spectra are restricted in practice to those atoms which have a relatively small quadrupole moment or have spin $^1/_2$ and hence no quadrupole moment. Most of the work on indirect spin-spin splitting carried out to date in the field of phosphorus chemistry has been on the interaction of hydrogen, fluorine, and phosphorus atoms which are covalently bonded into the same molecule or molecule-ion.

If two like atoms exhibiting nuclear spin are in exactly equivalent positions in a molecule or molecule-ion, indirect spin-spin coupling between them does not lead to resonance multiplets. Thus, in the hypophosphate ion, $(O_3P\text{-}PO_3)^{4-}$, there must be strong coupling between the two phosphorus atoms directly bonded to each other; but the nuclear magnetic resonance spectrum shows only a single peak. For the same reason, the pyrophosphate ion, $(O_3P\text{-}O\text{-}PO_3)^{4-}$, also shows only a singlet.

In the case where there are only two coupled nuclei and they are different either in position in the molecule or in atomic number, coupling between them leads to a doublet instead of a singlet line for each magnetic nucleus. For example, the phosphorus resonance of the phosphite ion, HPO_3^{2-}, is split into two peaks separated by about 0.38 gauss or 655 cycles/sec.; whereas, the hydrogen resonance is also a doublet with the two peaks separated by 0.154 gauss or 655 cycles/sec. In the general case where there are

three or more coupled nuclei, the quantum mechanical wave equation must be solved, and examples of the interpretation of complicated nuclear magnetic resonance spectra are given in the literature along with some general directions for their interpretation.[25]

There are certain cases, however, which are amenable to a simple interpretation. These result when the separations of the resonance frequencies estimated for the nuclei (assuming no coupling or coupling with another atom) are very large with respect to the separations between the multiplets due to the indirect spin-spin coupling. This is the case when several atoms of one element are bonded to an atom of another element. In this case, if there are n atoms of type A bonded to atom B, the nuclear magnetic resonance spectrum of B will show $n + 1$ peaks, with the relative area of the ith peak being given by the following formula, with both A and B having spin $^1/_2$

$$A_i = n!/[(i-1)!(n-i+1)!] \qquad \text{for} \qquad 1 \leqslant i \leqslant n+1 \qquad (2\text{-}13)$$

An example is found in phosphine, PH_3, for which the phosphorus spectrum (see p. 182) exhibits four peaks of relative areas 1-3-3-1 and the hydrogen spectrum exhibits a 1-1 doublet. In phosphine the hydrogen atom resonates at a very much higher magnetic field (or alternatively at a much higher frequency at fixed field) than does the phosphorus atom, so that the spin-spin splitting is very small in comparison. This behavior is also exemplified by the tripolyphosphate anion, $[O_3P\text{-}O\text{-}P(O_2)\text{-}O\text{-}PO_3]^{5-}$ in which the peak due to the two end-group phosphorus atoms exhibits a doublet structure because of coupling with the single middle-group phosphorus which, in turn, exhibits a 1-2-1 triplet because it is coupled with the two end-group phosphorus atoms (see p. 640).

Another example of simple interpretation is found in the case of the isohypophosphate anion, $[H\text{-}P(O_2)\text{-}O\text{-}PO_3]^{4-}$. The phosphorus spectrum of this anion exhibits three major peaks, all three of which are further split into 1-1 doublets (see p. 401). Two of the major peaks are attributable to a large splitting of the phosphorus to which the hydrogen is directly attached. Superimposed on this is a second, much smaller, splitting of these two peaks and of the peak due to the other phosphorus atom. This small 1-1 splitting is due to the coupling between the two phosphorus atoms. Since the centers of the resonance patterns due to each phosphorus atom lie close to each other, overlapping of the peaks would have prevented a simple interpretation had the large splitting of the one phosphorus nucleus

[25] H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, **35**, 65, 1060, 1487 (1957); W. Anderson and H. M. McConnell, *J. Chem. Phys.*, **26**, 1496 (1957); H. M. McConnell, A. D. McLean, and C. A. Reilly, *ibid.*, **23**, 1152 (1955).

been absent. Throughout the remainder of this book many examples of structure proofs involving indirect spin-spin coupling are given. Some special cases of unusual interest have been reported in the literature.[26]

In the preceding discussion of indirect spin-spin splitting, it was stated that this occurs when the nuclei in question belong to atoms which are covalently bonded into a nuclear structure. This can be said in another, more precise way[27]—in terms of the average length of time that these "bonded" atoms retain a fixed geometrical relation with respect to each other In cases where the rate of exchange of atoms between molecules is quite rapid, there will not be spin-spin coupling Thus, none of the weak hydrogen atoms on phosphoric acid couple with the phosphorus atom, since the rate of exchange of the hydrogens between different molecules of phosphoric acid and between the phosphoric acid and water is rapid with respect to the time constant of the nuclear magnetic resonance measurement These time constants can be calculated[26] and are of the order of magnitude of a second At this time, kinetic measurements of exchange phenomena involving phosphorus compounds have not yet been carried out by interpretation of the line broadening observed in the region at which the exchange rate is similar to the time constant of the resonance measurement Obviously, this technique holds considerable promise for the investigation of exchange rates which are difficult to study by other techniques

DIPOLE MOMENTS AND POLARITY OF MOLECULES

Measurement of the dielectric constant of solutions and gases shows that molecules which are unsymmetrical in shape or type of constituent atoms exhibit a dipole moment As might be expected, a part of the measured dipole is attributable to the polar character of the bonds in the molecule. This fact has led to a number of correlations between electronegativity difference and dipole moment [28,29] In general, these correlations have not proved to have much practical value because of other polarities which are difficult to calculate and hybridization of the nonbonding with the bonding electrons to give a concentration of electronic charge (sort of an abortive bond) in the direction in which the hybrid would normally exhibit a bond. Indeed, at the present time, it appears that the measured dipole moment of

[26] C. F Callis, J. R. Van Wazer, J N Shoolery, and W A Anderson, *J Am Chem Soc.*, **79**, 2719 (1957)

[27] F. Bloch, *Phys Rev*, **102**, 104 (1956)

[28] M. G Malone and A L Ferguson, *J Chem Phys.*, **2**, 99 (1934), also C. P Smyth, *J. Phys Chem*, **41**, 209 (1937), *J Am Chem. Soc*, **60**, 183 (1938).

[29] N B Hannay and C P Smyth, *J Am Chem Soc*, **68**, 171 (1946).

a molecule is the resultant of a number of vectors lying in four general classes: (1) moments due to the unbalance between the nuclear charge and the gross electronic charge of each of a pair of neighbor or nearest-neighbor atoms, especially with one atom being an electron donor, the other an electron acceptor; (2) σ-bond moments or, more simply, the unequal distribution of charge in a σ-bond between two atoms of different electronegativities; (3) electron redistribution due to π-bonding —a factor which often acts as a feedback to reduce the σ-bond moments, (4) the hybridization or abortive-bond moments,[41] and (5) the polarization or induced moments Although quantitative consideration of these factors is obviously hard to carry out, overlap moments have been calculated,[40] and the amount of ionic character in the bonds of alkali metal and hydrogen halides has recently been estimated correctly from dipole moments.[42] The ionic character of the bonds as calculated from the dipole moment data was found to agree well with the values obtained from nuclear quadrupole coupling constants

TABLE 2-9

Dipole Moments in Debyes of Some Triply Connected Molecules of Group V Elements

		N	P	As	Sb
		[3.1][a]	[2.2]	[2.1]	[2.1]
		N	P	As	Sb
		[3.1][a]	[2.2]	[2.1]	[2.1]
H	[2.2]	**1.47**[b]	**0.55** 0.55	**0.22** 0.16	**0.116**
C (phenyl)	[2.6]	0.26	1.15	0.57	0.0
I	[2.7]		0.00	0.96	1.58, 0.4
Br	[3.0]		0.61	1.60	2.47
Cl	[3.2]		0.78	1.97, 2.15	3.12
F	[3.9]	**0.234**	**1.025**	**2.82**, 2.65	

[a] Values in brackets, [ ], are electronegativities

[b] Values in boldface type come from microwave spectra, the other values come from dielectric constant measurements

Uninterpreted dipole moment data for a number of tetratomic molecules based on the Group V elements are given in Table 2-9. The values in boldface type are obtained from microwave spectra and accurately represent the

[40] R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949)

[41] C. A. Coulson, *Valence*, Oxford, 1952, p. 210

[42] W. Gordy, *Discussions Faraday Soc.*, **19**, 14 (1955)

dipole moments of the isolated molecules. The other values come from interpretation of dielectric constant measurements.

The large dipole moment of ammonia as compared to nitrogen trifluoride, even though the bond angles are about equal, has been explained in terms of some sp^3-hybridization.[31] This sp^3-contribution causes a concentration of negative charge (abortive bond) on the side of the nitrogen atom opposite to where the three hydrogen or fluorine atoms are attached. The dipole due to this abortive bond is opposed by the moments of the N—F bonds to give a low over-all dipole moment of 0.234, whereas the polarities of the N—H bonds are reversed as compared to the N—F bonds so as to give a high resultant moment of 1.47, when combined with the electron concentration on the opposite side of the nitrogen atom. Apparently there is a similar abortive bond on the phosphorus halides and phosphine, as evidenced by the zero moment of PI_3 as compared to PH_3 and PBr_3. A rough calculation indicates that the dipole moment of the abortive bond in the triply connected phosphorus compounds is about equal to the P—I bond moment.

The dipole moments of 1.76 and 2.13 debyes, determined by microwave spectroscopy, for POF_3 and PSF_3 correlate with the moments of the trihalides when the molecular moment is assumed to be due solely to the bond moments (including the abortive bond), and reasonable values for the P—O and P—S moments are derived. However, the moment of 2.40 found for $POCl_3$ from dielectric constant data does not fit into such an oversimplified scheme. Obviously, the considerable body of literature in which dielectric constant data on organic phosphorus compounds are simply interpreted in terms of structure by the use of only bond moment considerations is very suspect. In some cases, the authors (Arbusov, Kosolapoff, and other notables) may have been fortunate in that the component moments of which they were not cognizant cancelled each other. However, without a careful theoretical reinterpretation, such dielectric constant work should be ignored—as is done in this book.

Bond Angles and Ionic Character

As explained in Chapter 1 (p. 11), bond angles depend on the type of hybridization of the central atoms in a molecule. Thus, there is a preferred set of bond angles for any element corresponding to the hybrid state of lowest energy. For the phosphorus atom triply connected to other phosphorus atoms, the optimum bond angle has been calculated[33] to be 89°55′,

[33] L. Pauling and M. Simonetta, *J. Chem. Phys.*, **20**, 29 (1952). The best *spd*-hybrid is $\psi = 0.0685s + 0.9858p_z + 0.1530d_z$.

corresponding to the best *spd*-hybrid. Deviations from this angle can occur because of repulsion between the X atoms in the PX_3 molecule acting against the bending force constant of the P—X bond. The repulsion is due to the permanent charge on the ligated atoms due to polarity of the bonds and to van der Waals' repulsion. In the majority of triply connected phosphorus compounds, this repulsion has spread the bond angle to a fairly constant value of 101° ± 2° An exception is found in phosphine which has a bond angle of 93°. Presumably, this is attributable to the smallness of the hydrogen atom and a relatively high force constant for the P—H bond

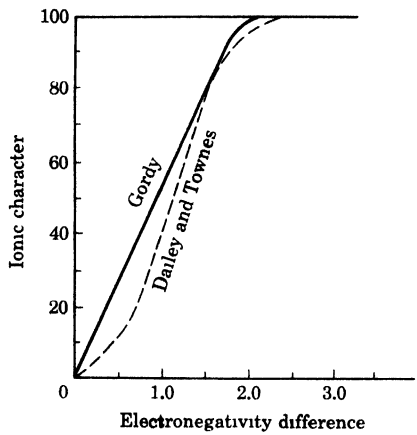


Fig. 2-6. Percentage of ionic character of the bonds in diatomic halides versus electronegativity difference of the bonded atoms as calculated from nuclear quadrupole coupling data.

In order to estimate the charge on the various atoms making up a molecule or molecule-ion, the ionic character or polarization of the bonds connecting the atoms must be known. The ionic character of a bond will obviously be related to the difference in electronegativity of the pair of bonded atoms; however, this relationship has not as yet been calculable from theoretical grounds. Rough estimates of the ionic character of the bonds in a number of diatomic halides have been made on the basis of dipole moments.[29] However, the correlations between electronegativity difference and ionic character based on these data have been superseded by more precise relationships based on the interpretation of nuclear quadrupole moment data in terms of ionic character of bonds.[32, 34] Because of

[34] B. P. Dailey and C. H. Townes, *J. Chem. Phys*, **23**, 118 (1955); B. P. Dailey *Discussions Faraday Soc.*, **19**, 255, 274 (1955).

difficulties in deciding the amount and kind of hybridization of the predominantly *s*-orbitals of the bonds studied, there is some deviation between the amount of ionic character calculated by Gordy (who assumed pure *s*-bonding) and by Dailey and Townes. However, as is shown in Figure 2-6, the two curves relating ionic character of the bond with the electronegativity of the bonded atoms are quite similar. Both relationships also indicate a much more pronounced change in ionic character with electronegativity difference than was surmised from the earlier dipole moment data.

From the electronegativities given in Figure 2-2, it is apparent that, in the majority of its known compounds, phosphorus is either electropositive to its neighboring elements (*viz.* F, O, N, Cl, Br, S, C, and I) or has the same electronegativity (*viz.* H and P). There are only a few cases where the phosphorus is more electronegative than the elements (*e.g.*, B, As, Si, and Al) bonded directly to it in stable molecular structures. According to the curves of Figure 2-6, the P—F bond should exhibit about 95% ionic character, with the phosphorus having the positive charge. Likewise, the P—O bond should have about 70% ionic character by the same criterion. However, in either case, the presence of π-bonding greatly reduces the ionic character of the σ-bond as estimated in this manner. Indeed, π-bonding can be considered as a "feedback" mechanism for reducing charge differences between neighboring atoms in the same molecule. From an approximate numerical treatment given by Pauling,[15] it appears that about three-quarters of the ionic character in the σ-bond from a quadruply connected phosphorus atom to a first row element and half of the ionic character in the σ-bond to a second row element is neutralized by π-bond formation. The curves of Figure 2-6 should thus be interpreted as maximum values for the ionic character of various bonds, with the presence of π-bonding reducing the ionic character to a lower value than the one indicated by Figure 2-6. Of course, such semiempirical correlations as Figure 2-6 must be considered as very rough approximations when applied to miscellaneous molecular structures more complicated than the diatomic halides. A much better approximation for the phosphorus-based molecular structures is given by available quantum mechanical treatments as applied to each specific case.[16]

IONIC RADII

Although phosphorus is always covalently bound to neighboring atoms in its compounds, much of the chemistry of phosphorus deals with ionized compounds in which the phosphorus-containing anion or cation is a more or less complex molecule-ion. Therefore, the radii of a number of ions

which may be of interest to the phosphate chemist are given in Table 2-10. In the case of the monatomic ions,[35] the tabulated values correspond to the coordination number of six, which is often found in ionic crystals. An increase in the coordination number over six leads to an increase in the radius (1.04r for an 8-fold and 1.09r for a 12-fold coordination). Likewise, a decrease in coordination number leads to a slight diminution of the ionic radius (0.95r for a 4-fold coordination which is rare for ions). The radii of molecule-ions exhibiting a center of symmetry is taken as the sphere having as radius the distance from the center of the assemblage to the point at which a monatomic counter-ion can most closely approach the most outlying atom in the assemblage. Under conditions of free rotation for the molecule-ion in question, this radius is the closest distance to which another ion of any size might approach

TABLE 2-10
Ionic Radii in A

		H^+	
		0 2	
O^{2-}	F	Li^+	Be^{2+}
1 40	1 36	0 60	0 31
S^{2-}	Cl^-	Na^+	Mg^{2+}
1 84	1 81	0 95	0 65
	Br	K^+	Ca^{2+}
	1 95	1 33	0 99
	I	Rb^+	Sr^{2+}
	2 16	1 48	1 13
		Cs^+	Ba^{2+}
		1 69	1 35
PO_4^{3-}, HPO_4^{2-} $H_2PO_4^-$		NH_4^+	
ca. 2.9		1 48	

Since all monatomic ions and many of the simpler molecule-ions exhibit spherical symmetry, the ions pack together like spheres. Thus, for crystals in which the radius ratio of cation to anion falls below 0.42, the small cations fit into the interstices between the anions which touch each other.[35] Because of the anion-anion repulsion due to like charges, the distance between the nuclei of the anions will be somewhat larger (a few hundredths of an A.) than the sum of the anion radii. The theory of ionic radii is well worked out, and the reader is referred to Pauling[35] for further detailed information.

[35] L. Pauling, *The Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithaca, N. Y., 1945, pp. 335–80.

NONBONDED RADII

The so-called "nonbonded" or van der Waals' radii of atoms are a measure of the internuclear distances between chemically saturated, un-ionized atoms. Thus, in liquid white phosphorus the P_4 molecules, within which the phosphorus atoms exhibit a bonded radius of 1.11 A., are separated by a P—P distance equal to 3.9 A., which is nearly exactly twice the nonbonded radius of phosphorus, 1.9 A. A collection of nonbonded radii is presented in Table 2-11.[35]

TABLE 2-11
Nonbonded Atomic Radii in A

	H 1.2		
C 1.7	N 1.5	O 1.4	F 1.4
Si 2.0	P 1.9	S 1.9	Cl 1.8
	As 2.0	Se 2.0	Br 2.0
CH_3 2.0			I 2.1

As has been shown in Figure 2-3, the nonbonded radii are approximately equal to the anionic radii in the case of the elements in Groups VI and VII of the periodic table. This is true because the bonded atom has the same number of electrons and presents the same face to the outside world in the direction away from its bond as does the equivalent ion in all directions. It should be noted that the nonbonded radii are only given to ±0.1 A. in Table 2-11, since these values are approximations to the equilibrium distances set up by dipole interactions which will depend in detail on the exact electronic configurations of the atoms, as well as the crystal geometry. However, the nonbonded radii are very useful for approximate calculations involving liquids and solids based on molecules.

SUMMARY

1. The electronic configurations of isolated atoms are closely related to the chemical behavior of these atoms, as exemplified by the periodic table of the elements.

2. The electronegativity of the elements decreases from top to bottom and from right to left in the periodic table.

3. The σ-bond radii of the atoms decrease from left to right within a row of the periodic table and increase from row to row when going down the table. The radii of negative ions are larger than the σ-bond radii of the same atoms, and the reverse is true for positive ions.

4. The heat of formation of a gaseous molecule from the constituent atoms in their un-ionized ground states can be divided among the bonds in the molecule to give "bond energies." These bond energies are composed of (1) a σ-bond part made up of a nonpolar contribution from each of the two atoms in the bond plus a polar contribution calculable from the electronegativity difference of the atoms and (2) a π-bond part equal to about 50 kcal./π-bond.

5. Atom-center distances can be treated in terms of nonpolar σ-bond radii of the atoms from which corrections must be subtracted for polarity and π-bonding.

6. The heats of formation and atom-center distances available for phosphorus compounds indicate a considerable amount of π-bonding in the compounds in which the phosphorus is tetrahedrally connected to its neighboring atoms and essentially no π-bonding in the other compounds.

7. Nuclear magnetic resonance data are in accord with the division of phosphorus compounds into the classifications based on molecular geometry and π-bonding. The interpretation of both chemical shifts and indirect spin-spin splitting is briefly explained for the compounds of phosphorus.

8. Dipole moments of unsymmetrical compounds of the Group V elements are discussed in terms of several major factors, and it is concluded that the simple interpretations of dipole moment data appearing in the organic phosphorus literature are highly suspect and not worthy of much notice.

9. Tables of the various atomic radii, of electronegativities, and of bond energy contributions are given for the common chemical elements.

CHAPTER 3

Systematic Chemistry of Phosphorus and Its Compounds

INTRODUCTION

For many years descriptive chemistry has been divided into two separate disciplines: organic chemistry and inorganic chemistry. Although the differentiation between these two disciplines originally came about because one of them was presumed to cover the chemistry of living things and the other of inanimate objects, it later developed that organic chemistry dealt with the compounds based on carbon, whereas inorganic chemistry covered all the other elements and their compounds.[1]

This distinction between the chemistry of carbon compounds and all of the rest of chemistry has been a worthwhile one since organic chemistry has been systematized in a very logical manner, whereas classical inorganic chemistry has been, to a great extent, somewhat of a hodge-podge of facts. Organic chemistry is characterized by the classification of compounds into a relatively small number of homologous series, and the development of synthesis methods whereby specific compounds of considerable complexity can be prepared according to previously written structures. Furthermore, complicated molecules can be taken apart piece by piece and their constitution determined through identification of the pieces. In many respects organic chemistry can be considered as a system of chemical architecture in which molecular structures are erected according to plans (diagrams of molecular structures).

On the other hand, most of the compounds which have been prepared in the inorganic field have been identified after they were made. Even though family relationships between inorganic compounds are sometimes described, these are seldom used by the practical chemist and are apt

[1] This transition occurred in the middle of the 19th Century. A key paper was the description of the formation of urea from ammonium carbonate by F. Wohler, *Ann. Physik*, **12**, 253 (1828); J. Liebig and F. Wöhler, *ibid.*, **20**, 393 (1830).

to be pedantic classifications with no practical value in the laboratory. Furthermore, a large group—perhaps even the majority—of known inorganic compounds are characterized only by their proximate analysis with their exact atomic arrangement being a mystery. Modern inorganic chemists are apt to think of their subject primarily in terms of high polymers, whereas the classical compendia[2] give the impression that practically all inorganic compounds are relatively simple structures of low molecular weight

In the remaining section of this volume (Chaps. 4–13), the descriptive chemistry of phosphorus and its compounds is covered in considerable detail. Throughout the remaining part of the book it becomes apparent that there are a number of homologous series in the chemistry of phosphorus and that, indeed, in many other respects the chemistry of phosphorus is quite similar to organic chemistry. In view of this there is considerable hope that phosphorus chemistry may some day be developed into as elegant a discipline as present-day organic chemistry. In this chapter, some of the high points of the descriptive chemistry of phosphorus and its compounds will be previewed, and some likenesses and differences between the chemistry of carbon compounds and that of phosphorus compounds will be examined In particular, an attempt will be made to answer the question "What makes a systematic chemistry?" In this chapter, literature references will not be given for the phosphorus chemistry that is previewed. The reader is requested to turn to the appropriate chapter in the later part of this volume for more detailed information and literature citations

ESSENTIALS FOR A SYSTEMATIC COVALENT CHEMISTRY

Using idealized organic chemistry as a prototype, the criteria for a systematic, covalent chemistry appear to be the following:

1. The individual compounds are sufficiently stable so that they do not change during the standard laboratory operations whereby they are made and characterized.

2. A limited number of elements serve as backbone atoms in building up complicated molecular structures. To this backbone are attached other atoms or groups of atoms which can be thought of as being in a peripheral

[2] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1922–37, Vols. I–XVI; P. Pascal, *Traite de Chemie Minerale*, Masson, Paris, 1931–34, Vols. I–XII; J N. Friend, *Textbook of Inorganic Chemistry*, Griffin, London, 1924–37, Vols. I–XI, *Gmelin's Handbuch der anorganische Chemie*, Verlag Chemie, Leipzig, 8th ed., 1924–56, all volumes

position. A wide variety of substitutions is allowed in these peripheral atoms or groups.

3. A reasonable small number of homologous series can be set up into which all of the compounds can be classified. It is assumed that the total number of compounds in the systematic chemistry in question is extremely large with thousands or millions of individual compounds having their existence established.

4. Positional synthesis methods are developed whereby desired molecular structures can be made at will.

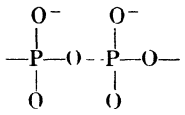
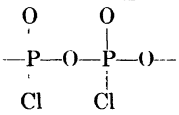
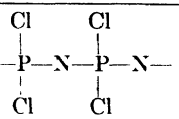
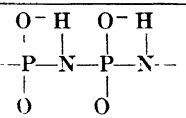
5. Unimers[3] and isomers are known, with differences between homologous series being pointed up by isomerism between the series.

The great majority of compounds in organic chemistry are not in true thermodynamic equilibrium with their environment and are often inherently capable of reorganizing into considerably more stable compounds However, for all practical purposes, the majority of organic compounds are stable (metastable substances). There are many known examples of thermodynamically unstable compounds (such as are to be found in a piece of wood) remaining unaltered for many thousands of years. This metastability in organic chemistry means that the rates of many conceivable chemical reactions are extremely slow. That is to say, high activation energies and/or low frequency factors must be associated with such rates. From the viewpoint of reaction-rate theory,[4] the activation energies and the heats of reaction or, alternatively, the free energies of the activated complexes and the free energies of the reactions can be diagrammatically represented in the form of potential energy surfaces.[4] In such a three-dimensional energy diagram, organic chemistry would appear as a very mountainous region, with numerous valleys and pockets being separated from each other by high ridges. It is the existence of these ridges that renders the organic compounds corresponding to the many energy valleys and pockets sufficiently metastable so that a systematic chemistry can be developed for them. There is one additional feature of the potential energy landscape corresponding to the chemistry of carbon and its compounds. This is the existence of a limited number of passes across the mountain ranges dividing one valley from another. In other words, the majority of organic reactions are characterized by a reasonably small number of activated com-

[3] J. K. Senior, *J. Chem. Phys.*, **19**, 865 (1951).

[4] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., Inc., New York, 1941, Chap. III, pp. 85–152. H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, John Wiley & Sons, Inc., New York, 1944, Chap. XVI, pp. 299–331.

TABLE 3-1
Homologous Series in Phosphorus Chemistry

	Phosphates	Phosphorus oxychlorides	Phosphonitrilic chlorides	Phosphimates
Typical pair of segments				
Number of phosphorus atoms in known				
Chains	1 to ca. 10^5	2, 3, and higher	large (10^2–10^5)	large (10^2–10^4)
Rings	3 to ca 15	?	3 to 7 (perhaps up to 10)	3, 4 (perhaps higher)
Chemistry	Polyelectrolyte	Polar polymer	Polar polymer	Polyelectrolyte
Condition of the amorphous solid containing long chains (no plasticizer)	Glass	Elastomer (?)	Elastomer	Glass
Remarks	Carefully investigated. See Chaps 8, 10, 11, and 12.	Recent as yet unpublished data See pp 247–249.	Well-known and long-established families of compounds. Fluorides and bromides also known. See pp. 309–317.	Known as derivatives of the phosphonitrilic chlorides. See pp. 319–320 and 837–843.

plexes through which the usual organic reactions proceed. The heat of formation of these activated complexes ranges from several to, say, 40 kcal./mole, whereas the activation energies for other more drastic processes (crossing over the mountain peaks rather than taking a pass) is of the order of magnitude of bond energies greater than about 50 kcal.

Although the thermodynamic properties of phosphorus compounds have received little study as compared to those of organic compounds, it is quite apparent from the chemistry that the potential energy surface is again quite mountainous with many pockets and valleys. However, there appear to be a rather large number of activated complexes available for any given compound, so that the valleys in the potential energy surface are separated by walls of about the same height as the passes found in the higher walls in the potential energy map corresponding to organic chemistry. This hypothesis is supported by the very common behavior exhibited by phosphorus compounds other than the phosphates in undergoing autoredox reactions upon being heated to give a number of compounds, ranging from phosphine to phosphorus to the lower oxyacids to the phosphates. In other words, once sufficient energy has been added to many phosphorus compounds, they simultaneously undergo a large number of reactions to give a variety of products

The predominant backbone element in organic chemistry is the carbon atom, and a large number of organic compounds are characterized by chains of carbon atoms Such catenation is relatively rare in the field of inorganic chemistry.[5] Perhaps the best-known example of inorganic catenation is found in the polysulfides. Although chains or rings of directly connected phosphorus atoms in which there are more than four phosphorus atoms have not been conclusively demonstrated, it is possible to interpret the chemistry of the phosphorus hydrides (see Chap. 5) in terms of homologous series of compounds in which phosphorus is the backbone and hydrogen is the peripheral element. Additional work is needed to prove this hypothesis.

In a large number of complicated organic compounds of biological significance, relatively small molecular structures (such as sugar moieties) are held together by C—O—C, C—N—C, and C—O—P linkages. From the viewpoint of organic chemistry these compounds are rather labile. The best typified and most fully populated homologous series in the field of phosphorus chemistry have properties quite similar to these organic compounds. Such homologous series are shown in Table 3-1. In all four of the examples of Table 3-1, the backbone of the structures consists of

[5] T. Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1952, pp. 569, 516-21.

phosphorus atoms alternating with either oxygen or nitrogen atoms, with the peripheral atoms being attached to the phosphorus. Of these homologous series, the chain and ring phosphates are the best known. The various structure-sensitive techniques which have been employed in studying the chain phosphates are listed in Table 3-2.

TABLE 3-2
Methods Used in Characterizing the Molecule-Anions of Chain Phosphates in Aqueous Solution[a]

Method	Year first used	Initial investigator
To determine molecular size		
End-group titrations	1944	Samuelson
Nuclear magnetic resonance peaks	1955	Van Wazer *et al*
Cryoscopy in $Na_2SO_4 \cdot 10H_2O$	1951	Siebert, reported by Weiser
Light scattering	1953	Strauss *et al.*
Dialysis and diffusion	1943	Karbe and Jander
Ultracentrifugation	1940	Lamm and Malmgren
Intrinsic viscosity in salt solutions	1950	Van Wazer
Limiting viscosity in water	1953	Strauss *et al.*
To determine molecular shape		
Flow birefringence	1953	Van Wazer *et al*
Anisotropy in electrical conductivity	1955	Eigen
To determine size distributions		
Solubility fractionations	1950	Van Wazer
Paper chromatography	1953	Ebel, Westman
Anion exchange chromatography	1953	Rieman *et al.*

[a] For a review of this work see C. F. Callis, J. R. Van Wazer, and P. G Arvan, *Chem Rev.*, **54**, 777 (1954).

In addition to the four groups of homologous series of phosphorus compounds shown in Table 3-1, there are a number of other homologous series which have been demonstrated only in vague outline. For triply connected phosphorus, there seems to be a very complicated system of several homologous series which are based on red phosphorus as the most highly polymerized member. Thus, the amorphous phosphorus hydrides appear to make up a family of compounds ranging all the way from the simplest member, phosphine, PH_3, through biphosphine, H_2PPH_2, to the three-dimensional network of red phosphorus in which there are occasional hydrogen atoms as end-groups. Also, a similar situation may well be true in the

phosphorus-oxygen system and in the phosphorus-oxygen-hydrogen system, in all of which oxygen atoms, hydrogen atoms, and hydroxyl groups act as terminators for variously sized networks of phosphorus atoms. In addition, oxygen atoms may also serve as linkages in such networks. The series of lower oxyacids of phosphorus now being developed by Blaser (see pp. 390–418) also appears to be proliferating into several homologous series of compounds. This possibility is discussed in considerable detail in the latter part of Chapter 7.

It should be noted that it is generally necessary to look for something before finding it; and very little effort has been expended in the past on looking for homologous series in the chemistry of phosphorus. Indeed, a large proportion of the pertinent organic and inorganic literature deals with compounds based on a single phosphorus atom. However, because of the present interest in the field, it is to be expected that a number of phosphorus-based homologous series will be discovered and an even larger number characterized within the next decade.

Little thought and effort have also been expended on developing methods of positional synthesis for phosphorus compounds. The main reason for this is that the classical chemists thought of phosphorus chemistry in terms of a relatively small number of very simple structures. It now turns out that many of the materials described in the classical reference books[2] in terms of a simple structure are really complicated mixtures of neighboring members in a homologous series. Graham's salt is a case in point. The chemistry of this complicated mixture of chain phosphates is now well known, see Chapters 8 and 12. Instead of being a relatively simple salt having a formula weight of 612 as supposed by a number of investigators at the beginning of the 20th century, Graham's salt really consists of a distribution of long-chain polyelectrolytes having formula weights ranging from about 5000 to about 50,000. Although very little work has been done on developing methods of positional synthesis for the compounds of phosphorus, this is a fertile field for further developments. Examples of preliminary studies along this line are the work of Todd and associates in synthesizing the adenosine polyphosphates (see pp. 633 and 660) and the preferential substitution by chlorine in the fluorochlorides of phosphorus (see p. 819).

Isomerism in phosphorus chemistry is another interesting problem which has been greatly neglected. Examples of two quite different homologous series of organophosphorus compounds, each having the empirical formula R_3PO are shown in Table 7-2, p. 354. A similar pair of isomeric series, having the empirical formula R_3PO_3, is described in Table 7-4, p. 376.

Structural isomerism is also discussed in the case of the phosphates in Chapter 8. However, much of this isomerism is purely hypothetical at the present time. Certain organic phosphorus chemists have been interested in optical isomerism and have resolved a number of compounds in which the phosphorus atom is optically active. These compounds are described on pp. 212, 288, and 308.

The ring phosphates, as well as the ring phosphonitrilic halides (see pp. 679 and 309, respectively), are examples of true structure polymers. Ring phosphates containing from 3 to about 8 phosphorus atoms per anion have been isolated, and about the same number of ring molecules are known for the phosphonitrilic chlorides. The empirical formulas of a number of other phosphorus compounds are best explained in terms of ring structures. Examples are the amorphous compound $(PO_2Cl)_x$, see page 248, and the apparently trimeric compound $[(CH_3)_2PAl(CH_3)_2]_3$, see page 199. With such rings, members of a homologous series of compounds exhibit exactly the same empirical formulas.

Quantum Mechanical Basis of a Systematic Covalent Chemistry

Many of the similarities and differences between the chemistry of carbon and its compounds and that of phosphorus and its compounds can be explained on the basis of fundamental concepts. Indeed, a great amount of detail in both fields can be simply related to certain broad conclusions derived from the quantum mechanical picture of matter. Because it is a first row element, carbon is restricted to *s*- and *p*-orbitals, with *d*- and higher orbitals being unavailable. Thus, carbon can have no more than four σ-bonds, corresponding to the tetrahedral sp^3-hybrid. In order to exhibit π-bonding, the carbon atom must go to lower coordination numbers, such as the planar triangular, sp^2-hybrid and the linear sp-hybrid. This explains the uniform "tetravalency" of carbon which was established by the classical chemists. Obviously, in order to obtain a π-bond it is necessary to lose a σ-bond. As a result, we can write the usual structural formulations in which each carbon atom has four lines leading from it, with "single," "double," and "triple" bonds being simply and graphically represented. The concept of fractional bonds is not particularly useful in organic chemistry, since it is possible to denote such a state of affairs in terms of bond resonance, an idea introduced by Kekulé in the middle of the 19th century.[6] The fact that carbon has four electrons in its valence shell means that, when it is present as an sp^3-hybrid, four electrons are donated by the

[6] A. Kekulé, *Ber.*, **2**, 362 (1869).

attached elements and four by the carbon. This common state of affairs for carbon chemistry led to the notion that the electron-pair bond in which each of the pair of bonded elements contributes one electron is somehow basically different from the bond in which but one element donates both electrons.[7]

For the second row elements, such as silicon, phosphorus, and sulfur, *d*-orbitals are available, although of higher energy than the *s*- and *p*-orbitals. There are a relatively small number of stable compounds of the second row elements in which *d*-orbitals seem to play a role in the σ-bond base structure. Examples are the hexafluorosilicate anion, SiF_6^{2-}, the hexafluorophosphate anion, PF_6^-, phosphorus pentafluoride, PF_5, and sulfur hexafluoride, SF_6, all of which are reasonably stable compounds. In these cases, the presence of high-energy *d*-orbitals in the σ-bond base structure is stabilized by the high electronegativity of the fluorine atom.

The sp^3-hybrids of the second row elements seem to exhibit quite uniformly a certain amount of π-bonding in which the *d*-orbitals of these elements are involved As pointed out in the previous chapter, phosphorus has approximately one-quarter to one-third π-bond per σ-bond when it is quadruply connected to the neighboring elements; but this π-bonding is usually lacking in the compounds in which phosphorus is either triply connected or exhibits a coordination number higher than four. Thus, when the coordination of phosphorus is reduced from that of the sp^3-hybrid to that approximated by p^3, π-bonding is generally lost! This behavior is just the opposite from that of carbon, for which it is necessary to go from the sp^3-hybrid down to the sp^2-hybrid in order to have π-bonding. It is interesting to note that, in $H_2(O_3PC_6H_5)$ and $H(O_2P(C_6H_5)_2)$, the π-bond structure of the phenyl groups does not seem to resonate with π-bonding between the phosphorus and the oxygen atoms (see p. 385). The deficiency of σ-bonding in the compounds in which phosphorus exhibits the symmetry corresponding to hybrids involving *d*-orbitals as well as the presence of π-bonding in the sp^3-hybrids indicates that it is unwise to carry the simple single, double, and triple bond ideas of organic chemistry over to phosphorus chemistry. Rather, the more sophisticated σ- and π-bond notation appears to be less misleading.

As already noted, one great difference between the chemistry of carbon and the *known* chemistries of the adjacent elements, such as boron, silicon, phosphorus, and nitrogen, is the extreme amount of catenation found in organic chemistry, as compared to the chemistry of the other elements.

[7] N. V. Sidgwick, *The Electronic Theory of Valency*, Clarendon Press, Oxford, 1927.

The existence of carbon-carbon chains is attributable primarily to the fact that the energy of a π-bond between two carbon atoms is roughly equal to the energy of a σ-bond between the same atoms.[5] On the other hand, the energy of a π-bond between nitrogen atoms appears to be considerably greater than the energy of a σ-bond, so that, in this case, chains of nitrogen atoms are unstable with respect to the formation of N_2 gas, in which there is considerable π-bonding. The case of oxygen appears to be very similar to that of nitrogen in that O_2 gas is more stable than chains of oxygen atoms. Azides readily give N_2; and peroxides readily give O_2

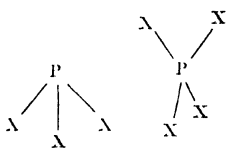
The fact that there are a large number of carbon compounds in which there are carbon-carbon chains and only a few established compounds in which there are phosphorus-phosphorus or silicon-silicon chains is attributable to the difference between carbon and phosphorus or silicon with respect to the mode of π-bonding. The great majority of methods for building carbon-carbon chains depend ultimately on some form of unsaturation (π-bonding).[8] In these procedures, the coordination number of the carbon is reduced from four to three or two and then is returned to four through attachment of another carbon atom to it. Of the various methods suitable for forming carbon-carbon bonds, only one, the Wurtz reaction, has been found to be applicable to the formation of phosphorus-phosphorus and silicon-silicon bonds. The Wurtz procedure does not depend on going from sp^3 to a lower hybrid plus π-bonds in the case of carbon but is a simple metathesis reaction. There are, of course, other techniques for making phosphorus-phosphorus and silicon-silicon bonds, but these have had little development because of the general lack of interest in positional inorganic synthesis and because most of the people thinking in terms of such syntheses are highly conditioned by their background of information in organic chemistry.[3]

KINDS OF PHOSPHORUS COMPOUNDS

As shown in Table 3-3, phosphorus is known to exhibit coordination numbers of 1, 3, 4, 5, and 6 in its compounds. Nearly all of the known compounds of phosphorus have coordination numbers 3 and 4. None of the compounds in which phosphorus is attached to a single atom (coordination number = 1) is stable under normal chemical conditions. The compounds in this class are diatomic molecules which are known primarily through their bond spectra.

[8] H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953). This article compares carbon chemistry with silicon chemistry and is couched in the terminology and thinking of organic chemistry.

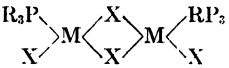
TABLE 3-3
Classification of Phosphorus Compounds

Number of attached atoms	1	3	4	5	6
σ-Bond hybridization for observed symmetry	p	p^3 with sp^3 character	sp^3	sp^3d	sp^3d^2
Directional characteristics	Linear	Trigonal pyramidal	Tetrahedral	Trigonal bipyramidal	Tetragonal bipyramidal
Geometry					
Number of known structures	ca 6	Thousands	Millions	ca 6	2
Stability under normal conditions	Unstable	Stable, but electron donor	Most stable as a class	Very reactive	Very reactive

The triply connected phosphorus compounds exhibit the pyramidal symmetry associated with p^3-hybridization. However, there apparently is a considerable amount of sp^3-character in many of these compounds, since their bond angles range around 100° instead of the theoretical 90° for a pure p^3-hybrid. By analogy to the chemistry of triply connected nitrogen,[9] it appears that the unshared pair of electrons on the phosphorus is in the form of what might be called an abortive bond because of the sp^3-character attributable to the hybridization of the phosphorus. As would be expected, the compounds of triply connected phosphorus act as electron donors, thereby converting the phosphorus into a quadruply connected atom in the resulting addition compound. Examples of such addition compounds are $H_3P \cdot BF_3$, $R_3P \cdot AlR_3$, $(R_3P)_2PtCl_2$, and $R_3P \cdot AuBr_3$ (see pp. 197–206). Some of these addition compounds exhibit isomerism. Thus,

[9] C. A. Coulson, *Valence*, Oxford University Press, Oxford, 1952, p. 210.

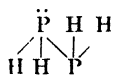
in the compound $(R_3P)_2PtCl_2$ the platinum is present as a dsp^2-hybrid in which the four bonds lie in a plane and are directed toward the corners of a square. This means that there are *cis* and *trans* isomers of $(R_3P)_2PtCl_2$ For a number of elements, such as mercury, cadmium, platinum, and copper, which can exhibit dsp^2-hybridization, compounds of the following type are known:



(3-1)

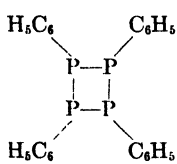
where M = Hg, Cd, Pt, Cu, and X = a halogen atom Obviously, this compound has three isomeric forms: a *cis*, a symmetrical *trans*, and an unsymmetrical *trans* isomer.

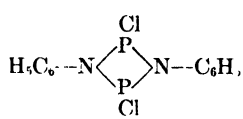
Most of the chemistry of triply connected phosphorus deals with compounds based on a single phosphorus atom. However, some complicated structures are known, and there is no reason that a large number of additional ones cannot be synthesized. Biphosphine (see p. 215) is an example of a compound in which two triply connected phosphorus atoms are bonded together.



(3-2)

Other examples are the halides, Cl_2PPCl_2 and I_2PPI_2 (see pp 234–235). Some published papers and recent work thus far unpublished indicate that the triply connected phosphorus compounds form stable four-membered rings. Some typical compounds are given below.





(3-3)

For the quadruply connected phosphorus compounds, the smallest unstrained ring appears to be composed of six atoms. This is to be expected for an sp^3-hybrid of phosphorus alternating with an atom such as oxygen or nitrogen which is so hybridized as to exhibit also a rather large bond angle (near the tetrahedral angle). However, for triply connected phosphorus, as well as triply connected nitrogen, a p^3-hybrid is possible, although in most of the compounds based on a single phosphorus or nitrogen atom, the angle tends to be nearer 100° than the 90° corresponding to a pure

p^3-hybrid. Presumably, there is very little energy involved in reducing the bond angle of the triply connected phosphorus atom to 90°, especially when the electronegativity difference between the phosphorus and the attached atoms (the neighboring phosphorus atoms in a four-membered ring) is zero. Just as the six-membered rings occur most commonly in the cyclic compounds based on quadruply connected phosphorus, so four-membered rings are found for triply connected phosphorus atoms. However, it is to be expected that, as the field of chemistry of the compounds based on a number of triply connected phosphorus atoms is broadened by continuing exploration, rings containing more than four triply connected phosphorus atoms will be discovered.

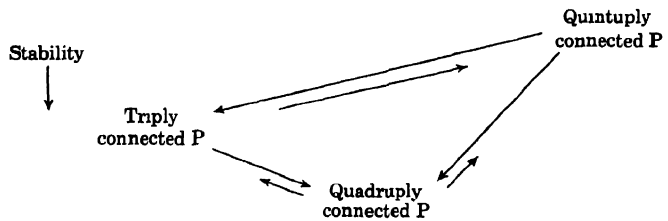


Fig 3-1 Schematic diagram showing relative energies of phosphorus exhibiting different coordination numbers

In the largest number and variety of its compounds, phosphorus exhibits the tetrahedral symmetry corresponding to sp^3-hybridization. It should be noted that the sp^3-hybrid is the most common for the first and second row elements of Groups III, IV, and V. Generally speaking, the compounds in which phosphorus is quadruply connected to its neighboring elements are more stable than those compounds in which phosphorus exhibits other coordination numbers (3, 5, and 6). This is diagrammatically illustrated in Figure 3-1. The reasons that the compounds in which phosphorus is quadruply connected are generally more stable than those in which the phosphorus is triply connected are:

1. Four bonds make contributions to the energy, rather than three.
2. As indicated in Chapter 2, the quadruply connected phosphorus compounds enjoy an energy contribution due to π-bonding which is usually not available to the compounds in which the phosphorus is triply connected.
3. Since phosphorus has five electrons, one of the four atoms connected to the phosphorus must be an electron acceptor, and such atoms usually contribute relatively large values to bond energies.

As shown by the examples in Table 2-5 (see p. 33), the phosphorus pentahalides exhibit heats of formation which are less than those calculated for five σ-bonds. In other words, it appears that the compounds in which there are more than four atoms connected to the phosphorus exhibit the symmetry of sp^3d- or sp^3d^2-hybridization without having the full complement of normal σ-bonds. This statement can be rephrased by saying that the compounds in which the d-orbitals of phosphorus must play a role in the σ-bond base structure exhibit a deficiency in energy because of the unavailability of the d-orbitals. Furthermore, as would be expected, the use of d-orbitals in the σ-bond base structure apparently makes these d-orbitals unavailable for π-bonding.

All naturally occurring phosphorus compounds are phosphates in which the phosphorus atom exhibits sp^3-symmetry. The phosphorus-containing minerals are orthophosphates, based on the isolated PO_4 group. In living organisms, polyphosphates as well as orthophosphates are found. In these structures the phosphorus atoms are also tetrahedrally surrounded by oxygen atoms, but chains are formed by the sharing of an oxygen between neighboring tetrahedra. The majority of known compounds based on a single phosphorus atom exhibit tetrahedral symmetry of the phosphorus.

In the homologous series of compounds listed in Table 3-1, the phosphorus atoms are all quadruply connected to their neighboring atoms. As might be expected from the above discussion, the individual members of these homologous series are reasonably stable compounds which can be studied by standard chemical techniques. Chains, rings, cage-like structures, planar networks, and three-dimensional networks are all known for compounds in which phosphorus is quadruply connected. In the majority of known structures in which there are at least several phosphorus atoms, the phosphorus atoms are not directly connected to each other but alternate with other atoms as in the examples given in Table 3-1. This is not necessary, however, and there is no reason why catenation between phosphorus atoms should not be present in molecular or ionic structures containing a number of such atoms. A few examples of catenation are known in which two quadruply connected phosphorus atoms are bonded to each other; *e.g.*, the hypophosphate anion $(O_3PPO_3)^{4-}$.

There are only a few known compounds in which phosphorus exhibits the trigonal-bipyramidal symmetry corresponding to sp^3d-hybridization. These are PBr_5, PCl_5, PF_5, several mixed pentahalides, and pentaphenyl phosphorus, $P(C_6H_5)_5$. Except for phosphorus pentafluoride, all of these compounds very readily tend to convert to a compound in which the phosphorus is quadruply connected. For example, in crystalline phosphorus

pentabromide there is a PBr_4^+ cation and a Br^- anion. Likewise, in ionizing solvents (high dielectric constant) with which they do not react, the phosphorus pentahalides ionize similarly to the way the pentabromide ionizes in its crystal. The vapors of phosphorus pentachloride and pentabromide dissociate into the respective phosphorus trihalides and the free halogen. In this case, phosphorus with a coordination number of 5 is converted into phosphorus with a coordination number of 3. The phosphorus pentahalides also form a number of ionized adducts in which a halogen atom is donated to an electron acceptor which becomes the anion, leaving the PX_4^+ group as the cation. Thus, the adduct between phosphorus pentachloride and aluminum chloride appears to be ionized into PCl_4^+ and $AlCl_4^-$ in nitrobenzene solution (see p. 241).

There are two known examples of compounds in which phosphorus exhibits the tetragonal bipyramidal coordination corresponding to an sp^3d^2-hybrid. One of these is the hexafluorophosphate anion, PF_6^-, which is reasonably stable in aqueous solution (see pp. 803–810). The other is the PCl_6^- anion which is observed in crystals of phosphorus pentachloride, along with PCl_4^+ as a cation (see p. 238).

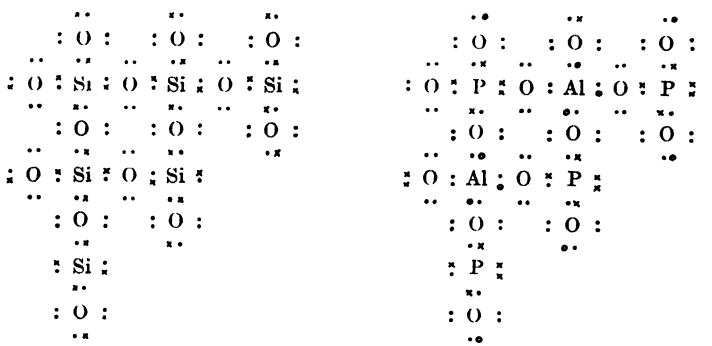
Several classes of organic phosphorus compounds have empirical formulas which might indicate that the phosphorus has a coordination number greater than 4. These are the so-called polyhalides, RPX_4, R_2PX_3, and R_3PX_2 (see pp. 262–263). However, what little evidence is available indicates that these compounds are derivatives of the phosphonium halides instead of the un-ionized phosphorus pentahalides (see p. 236). In other words, they are thought to be ionized in such a way that the phosphorus is in the cation. An interesting group of compounds is exemplified by $(C_6H_5O)_5P$ which formally can be classed as a derivative of a completely hydrated orthophosphoric acid (holophosphoric acid) in which the phosphorus atom would be surrounded by five —OH groups. However, the small amount of available evidence indicates that this compound is a quasiphosphonium salt of phenol, having the following structure $[P(OC_6H_5)_4]^+[OC_6H_5]^-$. An x-ray structure study on this compound or related ones is surely very desirable.

An interesting relationship based on the periodic table is found in the substitution of silicon atoms by pairs of aluminum and phosphorus atoms. Compounds or parts of compounds based on one aluminum and one phosphorus atom are isoelectronic with structures in which two silicon atoms replace the aluminum and phosphorus. Furthermore, the σ-bond radius of silicon is about half way between that of aluminum and that of phosphorus, as is its electronegativity. As a result, aluminum phosphide has

the same crystal structure as elemental silicon, as well as similar properties.

Probably the most complete known case of isomorphism is found between silicon dioxide, SiO_2, and aluminum orthophosphate, $AlPO_4$, or $Al_2O_3 \cdot P_2O_5$ (see pp. 553–555). Silicon dioxide exhibits three modifications —quartz, tridymite, and cristobalite—each of which has high and low temperature forms. The thermally induced transitions from one major modification to another are very sluggish so that quartz, tridymite, and cristobalite can all be kept at room temperature. However, the transitions between the high- and low-temperature forms of each modification are rapid. Aluminum orthophosphate also exhibits three major modifications which have the same crystal structures as quartz, tridymite, and cristobalite, respectively. Moreover, there are the same high- and low-temperature forms of each modification. The transitions between the major modifications of $AlPO_4$ are sluggish, whereas the transitions between high- and low-temperature forms are rapid! The parallelism appears to be complete, with the $AlPO_4$ transitions occurring about 50°C. lower than the SiO_2 transitions throughout the range from room temperature to the melting points near 1650°C.

Silicon dioxide exhibits a three-dimensional network structure as does $AlPO_4$. A distorted planar projection of segments of the structures is shown below to demonstrate that SiO_2 is isoelectronic with $AlPO_4$.



(3-4)

where × represents the electrons donated by the silicon or phosphorus atoms; • the electrons from the oxygens; and ○ the electrons from the aluminum atoms—with all electrons being fully equivalent.

This parallelism apparently continues over to the organic derivatives, where hexamethyldisilane, $(CH_3)_3SiSi(CH)_3$, is comparable to the addition compound between trimethyl aluminum and trimethyl phosphine, *i.e.*, $(CH_3)_3AlP(CH_3)_3$.

CHEMICAL REACTIONS

Generally speaking, the compounds of phosphorus are considerably more reactive than similar compounds of carbon. Thus, the carbon halides and hydrides are extremely stable, whereas the phosphorus halides hydrolyze readily in water, and biphosphine, for example, gives off phosphine and thereby undergoes condensation when allowed to stand at room temperature for several days. Likewise, P—O—P linkages in the phosphates undergo hydrolytic scission at about the same rate as C—O—C linkages in esters of organic acids. This rate is considerably faster than that corresponding to the hydrolysis of an ether. Generally speaking, the phosphorus compounds exhibit reactivities of the same order of magnitude as those of the majority of biologically active organic compounds, which are quite labile as compared to, say, the hydrocarbons under normal conditions.

Comparison of methane, CH_4, with silane, SiH_4, and phosphine, PH_3, points up the difference between first and second row elements. Although all three of these compounds undergo oxidation by similar branching-chain mechanisms, so that certain mixtures with oxygen are explosive and there are temperatures above which spontaneous ignition occurs, the various rate constants for methane are such that it must be ignited before burning in air at room temperature whereas phosphine burns spontaneously. Silane and phosphine are generally more reactive than methane, and this enhanced reactivity carries over to the second members of the respective homologous series. Thus, disilane, H_3SiSiH_3, and biphosphine, H_2PPH_2, are more reactive than ethane, H_3CCH_3.

The greater reactivity found in phosphorus chemistry as compared to carbon chemistry is readily explained in terms of electronic structure. The compounds based on triply connected phosphorus are quite reactive because the unshared pair of electrons offers a vantage point for the formation of an activated complex. Presumably, a number of reactions such as the readily observed exchange of halogen atoms in a mixture of different phosphorus trihalides occurs through a type of Walden inversion in which the point of attack is the unshared pair of electrons. It would be interesting, and probably quite fruitful, to compare reaction rates of triply connected phosphorus compounds with the natural inversion frequencies of the compounds (where the term inversion is used to refer to the molecular mode of motion similar to turning an umbrella inside out). Generally speaking, the compounds in which phosphorus is quadruply connected are less reactive than the compounds in which the phosphorus is triply connected. Examples are the phosphine oxides, R_3PO, which are quite un-

reactive as compared to the highly reactive organic phosphines, R_3P. Likewise, it is found that mixtures of different phosphorus trihalides exchange halogen atoms very readily, as compared to mixtures of phosphorus oxyhalides, POX_3.

By converting π-bonds into σ-bonds, a number of activated complexes of reasonably low energy are available for reactions of those compounds in which the phosphorus is quadruply connected. Indeed, a number of rate studies on such compounds have been interpreted in terms of an activated complex involving *d*-orbitals. Thus, the group of English physical organic chemists led by Ingold have shown that the quaternary ammonium hydroxides pyrolyze to give an unsaturated hydrocarbon plus a tertiary amine, whereas the equivalent quaternary phosphonium hydroxide gives a saturated hydrocarbon plus the phosphine oxide (see p. 212). As shown by the pair of equations below, the difference between these reactions has been attributed to the use of *d*-orbitals of the phosphorus in the activated complex. Naturally, *d*-orbitals are not available to nitrogen, which is a first row element

$$(RCH_2CH_2NR_3')^+(OH)^- \xrightarrow{\Delta} RCH{=}CH_2 + NR_3' + H_2O$$

$$(RCH_2CH_2PR_3')^+(OH)^- \rightleftharpoons [(RCH_2CH_2)P(OH)R_3'] \xrightarrow{\Delta} \quad \text{(3-5)}$$

activated complex

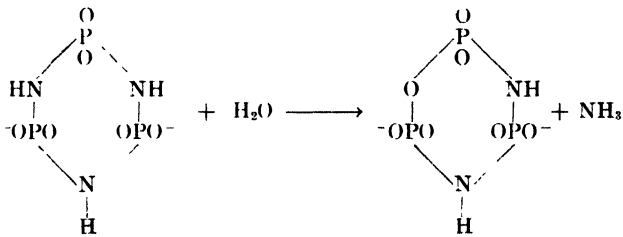
$$RCH_2CH_3 + R_3'PO$$

A similar state of affairs is shown in Figure 5-6 (p. 210) in which are compared the rates of formation of organic quaternary salts of an amine, phosphine, or arsine from the respective tertiary compound and ethyl iodide. It is found that over 95% of the quaternary phosphonium iodide is formed in 167 hr., as compared to 5% of the quaternary ammonium and 35% of the quaternary arsonium iodide. The fast rates of the phosphine and arsine as compared to the amine are attributable to the unavailability of the *d*-orbitals for the nitrogen, whereas the difference between the phosphine and the arsine reflects the usual diminution in reaction rate when going to elements of higher molecular weight in the same periodic group. Even in the case of phosphorus pentachloride, the kinetics of exchange of chlorine between it and elemental chlorine is believed to proceed via the formation of an activated complex having the sp^3d^2-configuration.

Discussions of the Michaelis-Arbusov rearrangement imply that it takes place via an activated complex in which *d*-orbitals are employed. In this rearrangement a triply connected phosphorus atom is converted into a quadruply connected atom, as indicated below in equation 3-6.

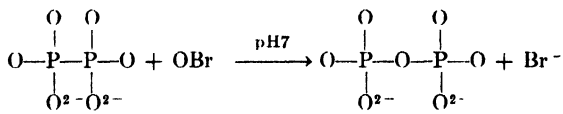
$$P(OR)_3 + R'X \rightleftharpoons [(RO)_3(R')PX] \longrightarrow R'PO(OR)_2 + RX \qquad (3\text{-}6)$$

There are a number of reactions of phosphorus compounds in which an atom is inserted between two phosphorus atoms or replaces another atom lying between two phosphorus atoms with essentially no scission of the linkage involved. In other words, the linkage appearing in the reaction product apparently forms before the linkage between the two phosphorus atoms in the reactant is broken. This undoubtedly occurs through use of the *d*-orbitals of the phosphorus atoms. It should be noted that the four-membered ring thus formed in the activated complex is not highly strained because bond angles in sp^3d- and sp^3d^2-hybrids are smaller than in the sp^3-hybrid. An example of such atom-substitution reactions is the replacement of imido groups by oxygen atoms in the hydrolysis of the cyclic metaphosphimates (see p. 840).



(3-7)

Another example is the oxidation of hypophosphate ion by bromine in sodium bicarbonate solution. This oxidation occurs very rapidly in neutral solution to give a 97% yield of pyrophosphate in about 15 min. The equation is shown below.

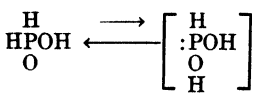


(3-8)

It is interesting to note that this reaction was once employed as a proof that the hypophosphate ion had a P—O—P linkage instead of a P—P linkage, as shown in equation 3-8, since it appeared inconceivable at that time that an oxygen could slip in between two directly bonded phosphorus atoms without the formation of a large proportion of compounds based on one phosphorus instead of two phosphorus atoms (see pp. 402–406). This example demonstrates how careful one must be in determining structures of compounds based on elements lying below the first row of the periodic table by use of reaction data. The structure of the product of a reaction is related to the structure of the activated complex and hence only in-

directly to the structure of the reactant. In organic chemistry where carbon, as a first row element has a limited selection of structures for the activated complex, it is much easier to relate the structure of a reaction product to that of the reactant.

The reaction kinetics for compounds based on quadruply connected phosphorus atoms can, on occasion, correspond to a shift to a triply connected phosphorus atom in the activated complex. Thus, the oxidation of hypophosphites by a number of different oxidizing agents, as well as the exchange of a bound hydrogen on a hypophosphite with the hydrogen of water, has been shown to proceed via an activated complex in which one of the hydrogen atoms directly attached to the phosphorus atom shifts over to an oxygen to form an —OH group. The reaction is shown below for the acid in un-ionized form.



(3-9)

activated complex

From kinetic studies, it appears that the activated complex is present only to the amount of a part per trillion!

In white phosphorus, P_4, and phosphorus sesquisulfide, P_4S_3, there are strained three-membered rings. Since in both cases the phosphorus atom is triply connected, the 60° angles in the strained ring correspond to "bent bonds" in which the bonding orbitals do not completely overlap. This strain explains the high chemical reactivity of the P_4 and the P_4S_3 molecules. Generally speaking, the elements around phosphorus in the periodic table are quite unreactive in their various allotropic forms, being like red phosphorus and black phosphorus. The unusually great reactivity of white phosphorus, liquid phosphorus, and phosphorus vapor to oxidation is attributable to the strained rings in the P_4 molecule.

Reorganization Equilibria

As described in the previous section, phosphorus compounds as a class are quite reactive, but yet the reactivity is not so great that the compounds tend to rearrange or react while being characterized. The moderately high reactivity means, however, that at reasonably elevated temperatures there should be a considerable amount of reorganization or exchange of parts between molecular structures. This is observed. As described in considerable detail in Chapter 12, the condensed phosphates, in which PO_4 groups are held together by the sharing of oxygen atoms to give complicated

structures, undergo reorganization in about the same way that organic polyesters reorganize. In other words, chains and rings of alternating phosphorus and oxygen atoms make and break, so that for any given ratio of ends to middles there will be a calculable distribution of molecular sizes ranging from species with molecular weights lower than the average through species having higher than average molecular weights. According to the Berzelius notation, the condensed phosphates can be considered as compounds in the system $xM_2O \cdot yP_2O_5$ where M stands for one equivalent of a cation or a functional group, such as the alkyl group in the ester of a condensed phosphate. In the phosphates the basic PO_4 groups, consisting of the phosphorus and its surrounding tetrahedron of oxygen atoms, must each obtain three additional electrons to exhibit completed valence shells. These electrons are obtained by sharing oxygen atoms between tetrahedra or by sharing or transferring electrons with the M atom (depending on whether the M is ionized or un-ionized). This means that at the end of a phosphate chain there are two M atoms, but that middles in a chain or in a ring exhibit only one M atom. Likewise, the phosphorus atom at a branching point in the structure will have no M associated with it. In other words, the M_2O/P_2O_5 mole ratio is the parameter that controls the relative amounts of structural units; *i.e.*, isolated PO_4 groups have three associated M's, end-groups have two associated M's, middle groups have one associated M, and branching points have no M atoms.

A theory for the distribution of the various structural units for given M_2O/P_2O_5 ratios is presented in Chapter 12 along with the distribution theory corresponding to a random reorganization of these parts between the various molecules and/or molecule-ions which are made up of these structural units. It is believed that the theory of reorganization given in Chapter 12 has extremely wide application in the general field of phosphorus chemistry. Thus, the polyphosphoryl halides in which there are P—O—P linkages appear to undergo reorganization (see pp. 248–249). For these compounds, the composition parameter M_2O/P_2O_5 (or its equivalent M/P) for the phosphates should be replaced by the parameter X/P, where X stands for the halogen. Likewise, the hypothesis is put forth in Chapter 5 (see p. 217) that a similar reorganization process, to which essentially the same mathematics would apply, occurs in the phosphorus hydrides. In this case, the M_2O/P_2O_5 composition parameter should be replaced by H/P. In Chapter 7 (see pp. 390–394) these ideas are qualitatively applied to the lower oxyacids of phosphorus. However, because of the complicated structures and the relatively large number of homologous series which can be formed in the system of lower oxyacids, there does not appear to be a

simple composition parameter which can be substituted for the M_2O/P_2O_5 mole ratio.

Presumably, the process of reorganization occurs readily for most inorganic compounds. Indeed, in many fields of inorganic chemistry, reorganization occurs so fast that it is difficult or even impossible to carry out a proper structure study. Presumably, there are a large number of different structures present in such substances as amorphous, hydrated ferric oxide. However, attempts to separate such structures and to characterize them have either not been attempted or been in vain because of the ease with which the individual structures can react and/or reorganize during the physical or chemical processes involved in the characterization. Thus, at least in the foreseeable future, no one is going to write a Beilstein about the structures present in a speck of rust! Many of the more complex compounds of phosphorus, like the esters of organic acids, lie in an intermediate position between the extremes of being highly stable or highly labile, so that reorganization and exchange phenomena will be observed in many cases, but at the same time the majority of compounds will be sufficiently stable so that their structures can be elucidated.

In many respects this is a happy concatenation of properties. It explains, for example, the predominant role that the phosphates play in biology. The biologists often speak of a large class of phosphates as "high-energy phosphates." The term "high energy" refers to the free energy of hydrolytic and similar processes, with the free energy being such that the equilibrium is essentially on the side of complete hydrolysis or some other pertinent reaction. In spite of the fact that the reactions can go essentially to completion, they proceed relatively slowly. In other words, the amount of activated complex in equilibrium with the reactants is probably very small. Phosphates play an important role in energy-transfer mechanisms and the storage of readily available energy in biological systems. This is to be expected for a group of compounds in which the atoms are held by strong covalent bonds but which generally have the capacity of being in equilibrium with a small amount of activated complexes for the various possible reactions.

The reorganization process has an effect of making certain reactions in the chemistry of phosphorus appear superficially simple. Thus, lead tetrapolyphosphate, $Pb_3P_4O_{13}$, is readily and quantitatively crystallized from a melt of the same over-all composition which exhibits a distribution of chain anions, including higher and lower members of the polyphosphate homologous series. Rapid reorganization allows the higher and lower polyphosphates to react together to form the tetrapolyphosphate, which is immedi-

ately withdrawn from the reorganizing system by the crystallization process. A similar occurrence is found when the ring phosphate, $Na_3(PO_3)_3$, crystallizes from the melt of the same approximate composition which consists of long-chain phosphates. Probably, such reactions as the cleavage of the P—O—P linkage in a pyrophosphate ester by hydrogen fluoride or water proceeds by a complicated reorganization process, when the mole fraction of the ester is greater than about 1–1.5. However, a simple chemical equation can be and is usually written for the over-all process.

BOND NOTATION AND CLASSICAL CHEMICAL THEORY

It is interesting to note that in all of the compounds based on triply connected and quadruply connected phosphorus, the phosphorus and its

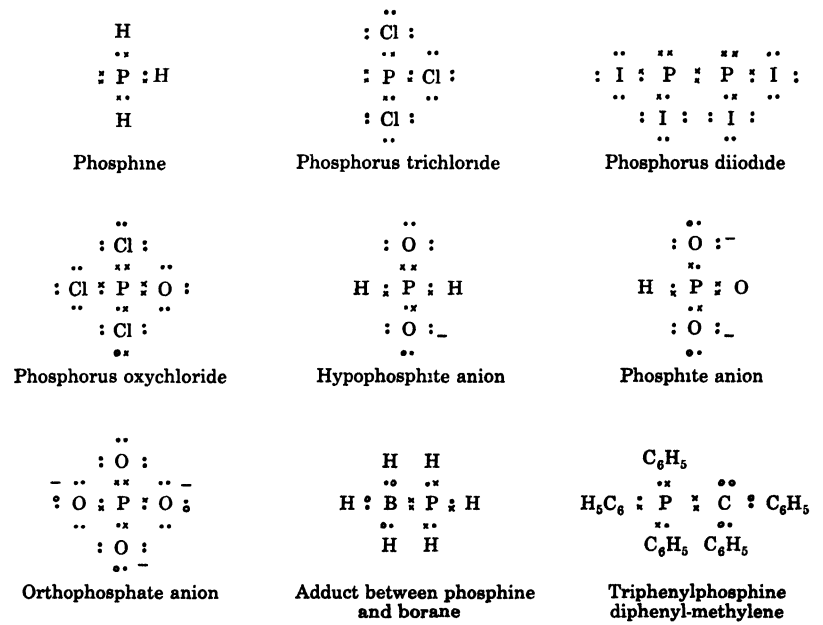
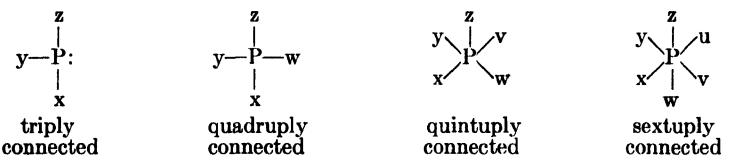


Fig. 3-2. Application of the Octet Rule to triply and quadruply connected phosphorus compounds.

neighboring atoms can be considered to obey the Octet Rule; *i.e.*, eight electrons can be assigned to the valence shell of each atom. Some examples to demonstrate this are given in Figure 3-2. In this figure, the electrons originating with the phosphorus atom are denoted by an ×; the electrons

from the neighboring atoms, such as an oxygen, by •; and the electrons from other atoms are denoted by ∘. Naturally, all of these electrons are truly indistinguishable, and different symbols are used for them only in order to keep ready count of their total number.

As described in Chapter 2, there is approximately one-quarter π-bond per σ-bond to phosphorus in the majority of the compounds in which it is connected to four neighboring atoms. This means that the bonding is part way between a single and double bond and hence is not truly represented by either the — or = notation. Likewise, it appears that in the compounds in which phosphorus is connected to five or six neighboring atoms, each connection corresponds to somewhat less than one σ-bond. This means that the best way to write formulas for phosphorus compounds is to use single lines between the phosphorus and its neighboring atoms as shown below. These lines represent chemical bonding but not necessarily single chemical bonds.



(3-10)

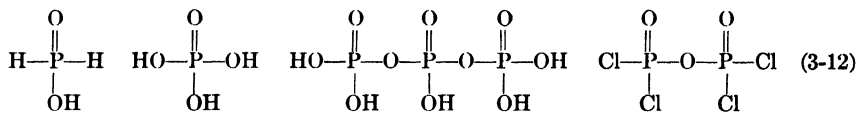
where u, v, w, x, y, and z represent the connected atoms.

Probably the oldest notation used in describing the compounds of phosphorus was the "double oxide" formulation developed by Berzelius. This is still a very useful way of representing a number of phosphorus-containing materials, since it gives the empirical composition with no inference as to the structure of the compound or, indeed, whether or not the material is a compound or a mixture of compounds. This notation is particularly useful in discussing mixtures in which structural reorganization has taken place. Some typical examples showing the use of the Berzelius notation are given below.

O HPH O H	O HPONa O Na	O O O NaOPOPOPONa O O O Na Na Na	O O ClPOPCl Cl Cl	(3-11)
3 $H_2O \cdot P_2O$ *or* $PH_3 \cdot 3\ H_2O \cdot P_2O_3$	2 $Na_2O \cdot H_2O\ P_2O_3$	5 $Na_2O \cdot 3\ P_2O_5$	4 $PCl_5 \cdot 3\ P_2O_5$	

According to the original valence-bond concepts, it was thought that hydrogen, the halogen atoms, and the alkyl radicals all have a single "chemical hook" or valence coming from them, whereas oxygen has two such

valences. The valence of phosphorus was considered as being variable so that the phosphorus would exhibit the proper number of valences to fit the valences of its neighboring atoms. Persons using the classical valence ideas today usually say that phosphorus must be either tervalent or pentavalent. According to this concept, quadruply connected phosphorus was quite universally considered to be "pentavalent," as indicated by the examples given below.


(3-12)

The major disadvantage of this classical valence bond notation is that it indicates differences which do not exist. In other words, the double bond between one oxygen and the phosphorus in the isolated orthophosphate anion is no different from the single bonds between the phosphorus and the other three oxygen atoms. Of course, the orthophosphate ion can be discussed in terms of a resonating system in which the double bond resonates between all four possible locations. For the orthophosphate ion, this fortuitously turns out to be a reasonably good approximation. However, it is believed that the safest and most logical notation is to employ only single lines to represent bonding and to discuss the π-character of this bonding in the text, rather than trying to give a graphic representation.

Perhaps the greatest fallacy resulting from use of the classical valence-bond theory of organic chemistry in phosphorus chemistry is the oversimplification of structures by use of multiple bonds. Examples of such false structures which have been shown in the literature are C_6H_5—P=P—C_6H_5, N≡P=NH, N≡PCl_2, and $(O=)_2$P—ONa.

A number of the classical authors used the term "valence" as a synonym for oxidation number. The oxidation number can be computed from the empirical formula of a compound, using the assumption that hydrogen, the alkali metals, and the alkyl radicals have an oxidation number of +1, the halides have an oxidation number of −1, oxygen has an oxidation number of −2, the alkaline-earth metals have an oxidation number of +2, etc. Then the oxidation number of phosphorus is that positive or negative quantity which leads to a value of zero for the sum of the oxidation numbers of all elements in the compound. In some cases, such as the phosphorus nitrides and phospham, it is difficult to assign an oxidation number to phosphorus, since this number is not fixed for either phosphorus or nitrogen. However, in unequivocal cases, it is found that phosphorus exhibits

oxidation numbers ranging from -3 to $+7$ and even higher—with occasional fractional oxidation numbers, such as $-1/2$ for the "compound" having the empirical formula P_2H. For compounds in which all of the atoms are completely ionized, these oxidation numbers tell how many electrons were transferred from the cations to the anions. Likewise, in the case of ionized compounds in which there are only a small number of atoms in the anion or cation, the oxidation numbers may also have a similar meaning. However, in the case of un-ionized compounds and most molecule-ions (ions containing a number of atoms, these atoms being bound together by covalent bonds), oxidation numbers have essentially no meaning. With the possible exception of a few metal phosphides, phosphorus is covalently bonded to its neighboring atoms in all of its compounds. Therefore, the oxidation number has no more significance in phosphorus chemistry than it does in organic chemistry, in which, for example, the carbon of methane, chloroform, and carbon tetrachloride exhibit oxidation numbers of -4, -2, and $+4$, respectively. The oxidation-number concept is not employed in organic chemistry to any extent, since it tends to confuse rather than to clarify thinking in this field. A similar state of affairs also obtains for phosphorus chemistry.

Sidgwick[7] and certain other authors employ what is often called the coordinate bond notation. According to this concept, covalent bonds in which both electrons have been furnished by one of the atoms sharing the electrons in the bond are different from bonds in which both of the atoms each contribute an electron. The electron-pair bond in which one atom has contributed both electrons is usually denoted by an arrow pointing from the atom which donated the electron pair. This type of bond has variously been dubbed a coordinate bond, a coordinate covalent bond, a semipolar double bond, a dative bond, and a covalent bond. This type of notation has, in some cases, at least a formal meaning, but for the majority of phosphorus compounds, it has no significance whatsoever. Thus, in the case of the orthophosphate ion, PO_4^{3-}, all physical evidence indicates that the four oxygens are equivalent although, according to the coordinate bond notation, one of the P—O bonds would be denoted by an arrow, with the other three being shown as a dash. If the coordinate-bond picture is used in this case, it is necessary to say that it resonates between all four positions. The same thinking is true for the ammonium ion, NH_4^+, in which one of the bonds ought to be written $N \rightarrow H$ according to coordinate bond notation. In this book the coordinate bond concept will be ignored, following the practice of modern theoretical chemistry.

Another concept occasionally still employed in theoretical discussions is

the formal charge on an atom. This formal charge is obtained by subtracting the number of unshared electrons and half the number of shared electrons from the periodic group number. This means that, ignoring π-bonding, phosphorus has a zero formal charge when there are either three or five atoms connected to it; a $+1$ formal charge for four connected atoms (with π-bonding being ignored); and a -1 formal charge for six connected atoms. The idea of formal charge is obviously closely related to the coordinate bond concept.

NOMENCLATURE

The naming of phosphorus compounds is in a very confused state, primarily because phosphorus chemistry is one of the oldest branches of this science. Occasionally, modern authors use names with an alchemical flavor, such as "Graham's salt," in the scientific literature. In this case, the alchemical-style term is employed because Graham's salt represents a random reorganization equilibrium for the composition in the Na_2O-H_2O-P_2O_5 system in which the Na_2O/P_2O_5 mole ratio equals 1.00 and $H_2O << Na_2O$. The innocuous name Graham's salt is the simplest way to represent all of these facts and at the same time to relate the modern literature to the considerable body of publications appearing on this subject over the last hundred years.

Another example of the use of outmoded concepts in nomenclature is found in the term "phosphorus pentoxide," as applied to the various compounds having the empirical formula P_2O_5. Before the general acceptance of the Avogadro hypothesis, water was written as HO and phosphorus pentoxide as PO_5. The name phosphorus pentoxide obviously fits the PO_5 notation and does not agree with the now accepted P_2O_5 notation which corresponds to the name diphosphorus pentoxide. Another interesting example of commonly accepted but confusing nomenclature occurs with respect to the calcium orthophosphates. Thus, the compound with the formula $Ca(H_2PO_4)_2$ is called monocalcium phosphate, the compound with the formula $CaHPO_4$ is called dicalcium phosphate, and the one with the formula $Ca_3(PO_4)_2$ is called tricalcium phosphate. These names are abbreviations of the once common terminology: calcium phosphate, monobasic; calcium phosphate, dibasic; and calcium phosphate, tribasic; respectively.

The most confused system of terminology occurs in the organophosphorus acids, their salts and esters. For example, the compound $R_2PO(OH)$ is called dialkylphosphinic acid in *Chemical Abstracts*, dialkylphosphonic acid

in Kosolapoff's[10] book, dialkylphosphonous acid according to British usage before 1952, and dialkylphosphinous acid in Beilstein. Furthermore, I have suggested that it might also be called either dialkylhypophosphorous acid or hydrogen dialkyldioxyphosphate. In this case, the trouble has arisen from too assiduous attention to nomenclature. Each name has a rational explanation. However, different people have used different names for the same compound and the same name for different compounds, so that it is impossible to understand the literature without seeing formulas or knowing beforehand to which school of nomenclature the author ascribed. The confusion lies in the endings -inic, -onic, -inous, and -onous, and it is my firm opinion that the only way the problem can be resolved is to drop these suffixes completely and replace them by other notation. This subject and proposed alternative notations are discussed in some detail in Chapter 7.

In spite of the remarks on nomenclature of the lower oxyacids of phosphorus given in Chapter 7, the leading philosophy employed in this book with respect to terminology has been

> What's in a name? That which we call a rose
> By any other name would smell as sweet.

Wherever possible I have attempted to use the best established name or the name now current in industry.

Probably the most glaring exception to this rule of thumb is the fact that the term "hexametaphosphate" is not employed in this book to describe either Graham's salt or the sodium phosphate glass for which the Na_2O/P_2O_5 mole ratio equals 1.1, even though this is common practice in industry. In this case, the term hexametaphosphate should not be employed, since it implies a completely incorrect chemical structure. Furthermore, there is a cyclic metaphosphate containing six phosphorus atoms which rightfully should be named hexametaphosphate. Therefore, this term has been reserved exclusively for the latter compound and is not applied to the sodium phosphate glasses.

Ideal Nomenclature

A perfect system of naming chemical compounds should indicate the number of atoms in the structure and their arrangement. It should also give some idea as to the presence or absence of ionization and the type of ionization. In silicate chemistry,[11] Greek prefixes are employed to indi-

[10] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950.

[11] G. W. Morey, *Encyclopedia of Chemical Technology*, R. E. Kirk and D. Othmer, eds., Interscience Encyclopedia, Inc., New York, 1954, Vol. XII, pp. 268–303.

cate the type of structure—ring, chain, three-dimensional network, etc. Greek prefixes of this type which are applicable to the chemistry of phosphorus compounds are listed in Table 3-4. It would be desirable to employ such terms in phosphorus chemistry. In addition, the chemical name of a compound should indicate the number of atoms connected to the various phosphorus atoms occurring in the structure.

The question of indicating the amount and type of ionization in the name of a compound becomes extremely involved in those cases where the compound is ionized under certain conditions and not under other conditions. For example, the halide in which there are five chlorine atoms to one phosphorus exists to a considerable extent as the un-ionized PCl_5 molecule

TABLE 3-4
Some Structure Types in Phosphorus Chemistry with Suggested Terminology

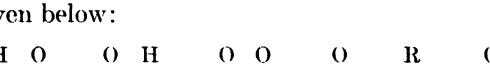
Type	Descriptive prefix	Greek root	Examples
Isolated group	neso-	νῆσος (island)	Na_3PO_4, PH_3, $POCl_3$
Chain	ina-	ἶνα (thread)	$Na_{n+2}P_nO_{3n+1}$, P_nH_{n+2}, $P_nO_{2n-1}Cl_{n+2}$
Ring	cyclo-	κῦκλος (ring)	$Na_nP_nO_{3n}$, $P_nN_nCl_{2n}$
Cage	clovo-	κλωβός (cage)	P_4O_6, P_4O_{10}, P_4S_3, P_4S_7, P_4S_{10}
Sheet	phyllo-	φύλλον (leaf)	$(P_2O_5)_n$, black P
Network	diktyo-	δίκτυον (net)	$(AlPO_4)_n$, $(BPO_4)_n$

in the vapor state. Obviously, the name phosphorus pentachloride is a good one for this molecule. However, in the crystal, ionization occurs to give PCl_4^+ and PCl_6^-. The most logical name for crystalline phosphorus pentachloride is thus tetrachlorophosphonium hexachlorophosphate. Phosphorus pentabromide is known to dissociate into PBr_4^+ and Br^-. If, under certain conditions, phosphorus pentachloride also should dissociate in this manner, it would then best be called tetrachlorophosphonium chloride. Although crystalline "tetrachlorophosphonium hexachlorophosphate" vaporizes to give "phosphorus pentachloride," the uninitiated would be hard put to guess that the two names referred to the same substance in different states.

Professor G. W. Schaeffer of Saint Louis University has suggested that an extension of the nomenclature[12] used for coordination compounds can be employed in naming compounds which are already known and might be expected in the chemistry based on quadruply connected phosphorus. This system of nomenclature uses three stems: *phosphonium* for positively charged molecule ions, *phosphorus* for neutral molecules, and *phosphate* for negative molecule ions. In the cationic structures, hydrogen is not explicitly designated. In the neutral and anionic structures, all ligands are explicitly accounted for. In this system of nomenclature, backbone atoms having a coordination number less than four are preferably treated as bridging atoms, which bear the prefix μ. Bridging oxygens are called "μ-oxo," and peripheral oxygens are called "oxy." Furthermore, the charge of an anion or a cation is always denoted by an Arabic number, followed by the appropriate plus or minus sign, in parentheses behind the name of the ion.

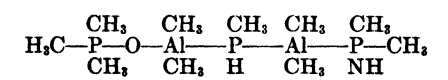
The nomenclature of simple structures is shown by the following examples: $[Cl_3P{-}{-}PCl_3]^{++} + 2Cl^-$ is called hexachlorodiphosphonium (2+) dichloride; $H^+ + [R(H)PO_2]^-$ is named hydrogen alkylhydrodioxyphosphate(1−) or, less preferably, alkylhydrodioxyphosphoric(1−) acid; and $RPO(OR)_2$ is called alkyl(dialkoxy)oxyphosphorus. This last item, $RPO(OR)_2$, could also be named as an ester, in which less preferable case it would be designated as dialkyl alkyltrioxyphosphate(2−).

The naming of a more complicated, hypothetical ionized phosphorus compound is given below:



8-alkyl-1,4-dihydro-heptadecoxy-*tria*-[2,4,6,7,8-μ-pentoxononaphosphate](8−) anion (3-13)

Un-ionized compounds can also be named by an extension of the "oxa-aza" system[13] in which various carbon atoms (and, indeed, *all* carbon atoms) of a hydrocarbon structure may be substituted by other atoms such as phosphorus (denoted as "phospha" in this system). The following structure of an "adduct" type of hypothetical compound is named according to (a) the coordination-compound notation, and (b) the oxa-aza notation.



[12] W. C. Fernelius, Chemical Nomenclature, *Advances in Chem. Ser.*, **8**, 9 (1953), published by the American Chemical Society, Washington, D. C.

[13] A. M. Patterson, L. T. Capell, and M. A. Magill, *Chem. Abstr.*, **39**, 5888 (1945).

Coordinate-compound name

5-imido-1,1,1,2,2,3,4,4,5,5-decamethyl-3-hydro*ina*-[1-μ-oxo-2,4-dialuminum-1,3,5-triphosphorus]

Oxa-aza name

7-imido-2,2-4,4,5,6,6,7-octamethyl[4,6-dialumina-3-oxa-2,5,7-triphosphaoctane]

(3-14)

It should be noted that all of the methyl groups are considered as ligands in the inorganic coordination-compound name; whereas, the carbons of two methyl groups are considered as chain atoms in the extended oxa-aza system.

Uncharged compounds based on triply connected phosphorus are probably best named as derivatives of phosphine or polyphosphines. Anionic or cationic structures in which there is one or more triply connected phosphorus atoms are not presently known and may not exist, so the problem of their nomenclature will not be touched upon here. Since the number of structures in which phosphorus is connected to more than four ligands is severely limited because of the use of *d*-orbitals in the σ-bond base structure, trivial names are probably quite satisfactory for this group, and there is no need – at least at the present state of knowledge – to spend effort on a systematic nomenclature for them.

CHAPTER 4

Elemental Phosphorus and the Metal Phosphides

HISTORY

Although an Arabian alchemist[1] named Alchid Bechil probably discovered phosphorus as early as the 12th century, the discovery of the element is usually attributed to Hennig Brandt, who was said to be an impoverished merchant seeking to restore his wealth by converting base metals into gold. During his alchemical experiments with urine, Brandt discovered white phosphorus,[2] probably in 1669. An 18th century representation of the discovery of phosphorus is shown in Figure 4-1.[3] For many years, the manufacture of elemental phosphorus was kept highly secret, because of the mysterious ability of white phosphorus to glow and burst into flame when exposed to air.

The name phosphorus—from φῶs, light; φέρω, I bear—was first applied to all substances which glowed in the dark but was later restricted to this element, which originally bore such names as phosphorus mirabilis and noctiluca consistens.

ELEMENTAL PHOSPHORUS

Preparation of Phosphorus

Elemental phosphorus can be prepared by reduction of practically any phosphorus-containing compound. The earliest preparations of phosphorus were obtained from urine, which was boiled down to a syrupy consistency and then distilled after being admixed with sand or charcoal. Phosphorus has been prepared by heating various phosphates, such as phosphoric acid or the calcium phosphate of bones, with charcoal. All of the phosphorus which is commercially produced at the present time comes from the reduction of phosphate rock with coke in an electric furnace. An approximate equation for the over-all reaction is given on page 95.

[1] F. Hoefer, *Historie de la chimie*, Paris, 1843, Vol. 2, p. 183.
[2] H. Peters, *Arch. Geschichte Naturw.*, **4**, 206 (1912); *ibid.*, **7**, 92 (1916).
[3] F. W. Shurlock, *Science Progr.*, **17**, 432 (1923).

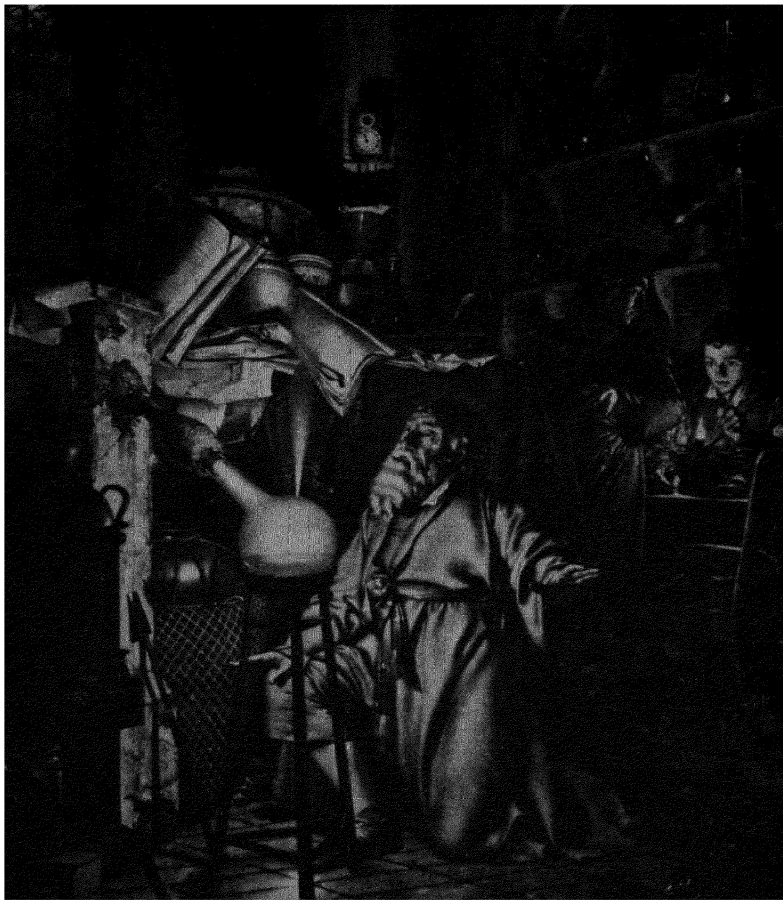


Fig. 4-1. A painting by Joseph Wright (1734–1797) showing a contemporary picture of an alchemist working with phosphorus. The small hole and jet of luminous vapor appearing in this picture are not the product of the artist's imagination but have been described in the literature of the early 18th century, the following translation from a French work of the time is reported by F. W. Shurlock, *Science Progr.*, *17*, 432 (1923).

"Phosphorus is a kind of sulphur composed of a peculiar acid united with phlogiston. This matter is extremely fusible, as we have seen. It has, like sulphur, two kinds of inflammation, one very weak, emitting a flame not powerful enough to kindle other combustible matters but sufficient for the gradual consumption and burning of its own phlogiston, the other is vivid, brilliant, and strong, accompanied with decrepitation and capable of kindling instantly any combustible matter. These two flames of phosphorus are easily distinguishable during the distillation of it, when the small hole in the receiver is unstopped; for, when the vessels are not too much heated, the flame which issues through the hole is luminous in the dark but does not kindle combustible matter; it may be touched without danger, and it only renders the hands that touch it luminous." (Courtesy Fisher Scientific Co.)

$$(4 + 4y)\ \underset{\text{fluorapatite}}{Ca_5F(PO_4)_3} + (20x + 1 - 9y)\ \underset{\text{silica}}{SiO_2} + (30 + 30y)\ \underset{\text{coke}}{C} \longrightarrow$$
$$20\ [CaO \cdot xSiO_2 \cdot yCaF_2]_{\text{slag}} + (1 - 9y)\ SiF_4\uparrow + (30 + 30y)\ CO\uparrow + (3 + 2y)\ P_4\uparrow \qquad (4\text{-}1)$$

where $x \approx 1$ and $y \leqslant 1/2$.

When there is a large amount of finely divided carbon, the reaction shown in equation 4-1 will proceed at measurable rates at temperatures as low as 1100°C.[4] However, in an electric furnace, the reaction is usually carried out at temperatures near 1450°C., where the slag melts. On the other hand, low-temperature reduction to elemental phosphorus of certain heavy-metal phosphates can be achieved with hydrogen. Thus, the reduction[5] of bismuth phosphate, $BiPO_4$, to bismuth and elemental phosphorus can be carried out at 425°C. Lead phosphate and antimony phosphate are similarly reduced to elemental phosphorus by hydrogen at 575° and 450°C., respectively.

Diatomic Phosphorus Vapor

At temperatures above 800°C., phosphorus vapor, which is usually in the form of P_4 molecules, is measurably dissociated into P_2 molecules. The P_2 molecule has been studied extensively by spectrographic means. The spectrum of this molecule has been measured in emission (especially in discharge tubes with hydrogen as the carrier of the discharge), in fluorescence, and in absorption. The spectrum exhibits a very extensive system of single-headed bands which are degraded to the red and extend throughout the ultraviolet. The large number of bands of about equal intensity is a characteristic feature of this spectrum, which corresponds to the transition $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$, ground state. From the rotational constants for the P_2 molecule, the equilibrium values[6] have been obtained for the moment of inertia, $I_e = 92.36 \times 10^{-40}$ g.-cm.^{2}, and for the internuclear distance, $R_e = 1.895$ A. The vibrational energy levels[7] of the P_2 molecule are represented by the equation

$$E_v/hc = 780.43\ (v + 1/2) - 2.804\ (v + 1/2)^2 \quad \text{in cm.}^{-1} \qquad (4\text{-}2)$$

which corresponds to an equilibrium frequency of 780.43 cm.$^{-1}$. The P_2 molecule dissociates into phosphorus atoms of ground state $^4S_{3/2}$ and nuclear

[4] J. W. Lefforge, unpublished work at the Monsanto Chemical Co.; also see ref. 98.

[5] J. C. Hutter, *Ann. chim. (Paris)*, **8**, 450 (1953).

[6] G. Herzberg, L. Herzberg, and G. G. Milne, *Can. J. Research*, **18A**, 139 (1940).

[7] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Co., Inc., New York, 1945.

spin $^1/_2$, with a dissociation energy[8] of 116.0 kcal./mole of P_2 at absolute zero. Since the phosphorus atoms recombine by way of collisions in the gas phase to give P_2, it appears[9] that atomic phosphorus cannot be obtained or kept for more than a momentary time outside of a discharge.

Tetratomic Phosphorus Vapor

Electron diffraction studies[10] show that the gaseous P_4 molecule is a regular tetrahedron, as depicted in Figure 4-2—with a P—P distance of 2.21 ± 0.02 A. and a moment of inertia about any of its three major axes of 2.51×10^{-40} g.-cm.^{2}. Quantum mechanical calculations[11] show that there are "bent bonds" in the P_4 molecule. The bond angle of an unstrained

Fig. 4-2. The configuration of the P_4 molecule

P—P—P linkage should be about 90°. However, in the P_4 molecule it is 60°, so that a strain energy of 22.8 kcal./mole of P_4 results, according to Pauling and Simonetta. A pd^2 hybrid bond[12] exhibits the proper bond angle near 60°, but the use of two *d*-orbitals requires very much more energy than does the "bending" or delocalization of the predominantly *p*-bonds with some *s*- and *d*-character. The calculations indicate that the unshared pair of electrons show predominantly *s*-character.

At temperatures below 800°C., the degree of dissociation of the P_4 vapor into P_2 molecules is essentially nil, and at this temperature there are only a few per cent dissociated, depending on the pressure. For the range from 900 to 1200°C., the following equation gives the pressures in atmospheres,

[8] See ref. 7, also A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules*, John Wiley & Sons, Inc., New York, 1947.

[9] N. M. Gopshtein and S. Z. Roginskiĭ, *J. Phys. Chem.* (*U.S.S.R.*), **7**, 587 (1936).

[10] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *J. Chem. Phys.*, **3**, 699 (1935).

[11] L. Pauling and M. Simonetta, *J. Chem. Phys.*, **20**, 29 (1952); W. E. Moffitt, *Trans. Faraday Soc.*, **44**, 987 (1948). Also see M. Mashima, *J. Chem. Phys.*, **19**, 1216 (1951).

[12] J. R. Arnold, *J. Chem. Phys.*, **14**, 351 (1946).

p_2 and p_4, of the diatomic and tetratomic molecules, respectively, as a function of the absolute temperature, T:

$$\log K_{atm} = \log (p_2^2/p_4) = 7.5787 - 11489/T \qquad (4\text{-}3)$$

The thermodynamic constants of both P_2 and P_4 vapor are given in Appendix C. Equation 4-3 is based on the vapor-density measurements of Stock, Gibson, and Stamm,[13] whose calculations only in terms of P_2 and P_4 molecules are in accord with spectroscopic data which show that monatomic phosphorus comprises less than 0.1% of the vapor at 1500°C. The heat capacity[14] of the P_2 vapor at 25°C. is 7.63 cal./°C.-mole, whereas that for the P_4 vapor is 16.0 cal./°C.-mole at the same temperature. The variations[14] of heat capacity and heat content of the P_2 and P_4 gases with temperature, as well as other thermodynamic data, are given by Farr.[15]

Dissociation of P_4 vapor into P_2 vapor can occur on surfaces such as tungsten. At low temperatures where the gas-phase dissociation of P_4 into P_2 is small, oxidized tungsten surfaces do not show this effect,[16] whereas clean tungsten does.

Oxidation of Phosphorus Vapor

The most important reaction of elemental phosphorus is oxidation. The oxidation of phosphorus vapor with air or oxygen has been extensively investigated.[17] Indeed, it is study of this phenomenon which led to the development of the theory of branching-chain reactions by Semenoff.[17] According to this theory, there are upper and lower critical pressures of oxygen for a given pressure of phosphorus. Between these critical pressures, ignition of the phosphorus vapor occurs; but, outside of this range of oxygen pressures, the rate of oxidation is very slow. The lower critical pressure, $p_{O_2}^{l}$, is—to a first approximation—inversely proportional to the pres-

[13] A. Stock, G. E. Gibson, and E. Stamm, *Ber.*, **45**, 3527 (1912).

[14] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," *Nat. Bur. Standards (U.S.) Circ.* 500, **72**, 570 (1952).

[15] T. D. Farr, *Tennessee Valley Authority Chem. Eng. Report No.* 8, 2–17 (1950), published by U. S. Govt. Printing Office.

[16] H. W. Melville and S. C. Gray, *Trans. Faraday Soc.*, **32**, 271 (1936).

[17] For a review see N. Semenoff, *Chemical Kinetics and Chain Reactions*, Clarendon Press, Oxford, 1935, pp. 163–99; *Chem. Rev.*, **6**, 347 (1927). Also see W. Jost, *Explosion and Combustion Processes in Gases*, trans. from 1935 ed. by H. O. Croft, McGraw-Hill Book Co., Inc., New York, 1946, Chapt. VIII, esp. pp. 283–91. More recent data are reviewed by D. M. Yost and H. Russell, *Systematic Inorganic Chemistry*, Prentice-Hall, Inc., New York, 1946, pp. 168–75; F. S. Dainton, *Trans. Faraday Soc.*, **43**, 244 (1947). Also see ref. 18.

sure, p_{P_4}, of phosphorus vapor and the square of the diameter of the containing vessel. Also it is lowered by the addition of inert gases and is independent of temperature. These relationships are shown by the following equation, in which μ is a factor depending on the coefficient of diffusion of oxygen in the added inert gas ($\mu = 0.13$ for He and 0.84 for CCl_4).

$$p_{O_2}{}^{l} p_{P_4} \left[1 + \frac{\mu p_x}{p_{O_2}{}^{l} + p_{P_4}} \right] d^2 = k_l \tag{4-4}$$

where p_x is the pressure of the inert gas, and k_l is a constant.

On the other hand, the upper critical pressure, $p_{O_2}{}^{u}$, of oxygen is proportional to the pressure of the phosphorus vapor, as shown by the following equation:

$$p_{O_2}{}^{u} / p_{P_4} = k_u e^{E_1/RT} \tag{4-5}$$

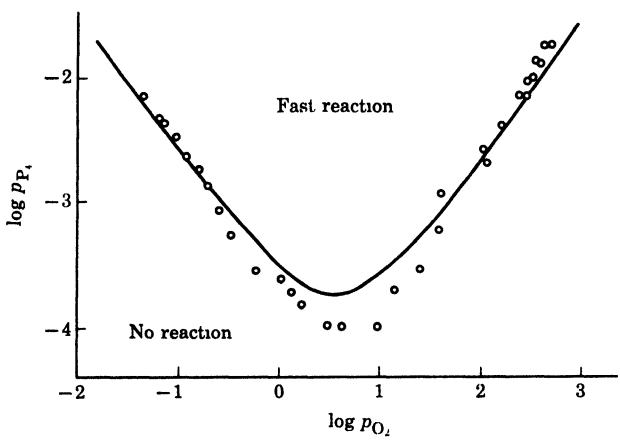


Fig. 4-3. The critical pressure for the oxidation of phosphorus.[17] The curve corresponds to predictions of the theory, and the points are experimental. Pressures in mm. of Hg

The value of E_1 in the above equation is very small (<1 kcal.). However, it is noted that as the temperature is raised, $p_{O_2}{}^{u}$ decreases slightly Inert gases also affect the upper critical pressure to a small amount, and it is raised appreciably by addition of small amounts of ozone. A comparison of theory with experiment is shown in Figure 4-3, where the upper and lower critical pressures of oxygen are plotted against the pressure of the phosphorus vapor, with no inert gas being present.

The slow reaction below the lower critical pressure seems to follow laws very similar to those found to govern the reaction in the explosion region.

Thus, the slow rate of reaction below the critical pressure, when the reaction was induced by a glowing tungsten filament, was found to be given by the following expression, in which the activation energy, E, equals 16 kcal.

$$-\frac{dp_{O_2}}{dt} = k_{O_2} p_{P_4} \left[1 + \frac{\mu p_x}{p_{O_2} + p_{P_4}}\right] d^2 e^{-E/RT} \tag{4-6}$$

The chain reaction involved in the glow oxidation of phosphorus vapor has been discussed in a recent paper.[18] It consists of the following sequence of reactions:

$$P_4 + O_2 \longrightarrow P_4O + O \tag{4-7}$$

$$P_4 + O + M \longrightarrow P_4O + M \tag{4-8}$$

where M is another atom (which can be a phosphorus or oxygen atom). In the general case, M may not always be necessary.

$$P_4O_n + O_2 \longrightarrow P_4O_{n+1} + O \tag{4-9}$$

where $n = 1, 2, \ldots 9$.

$$O + O_2 + M \longrightarrow O_3 + M \tag{4-10}$$

$$O + X \longrightarrow \text{Stable product} \tag{4-11}$$

where X is a "poison" to the reaction.

$$O + \text{Wall} \longrightarrow \text{Adsorbed oxygen} \tag{4-12}$$

The experimental data indicate that reaction 4-7 has no activation energy; *i.e.*, it is independent of temperature. The formation of a P_4O intermediate probably does not involve the rearrangement of P—P bonds but is thought to result from the sharing of one of the unshared pairs of electrons in the P_4 tetrahedron. The energy of activation of reaction 4-10 is 4.3 kcal./mole. The ozone formed in this reaction may enter into the chain of reactions in a way not shown by these equations.

The final product of the oxidation of elemental phosphorus is primarily phosphorus pentoxide, P_4O_{10}, plus some phosphorus trioxide, P_4O_6, as well as small amounts of other oxides and the various oxyacids of phosphorus produced by traces of moisture. Chapter 6 should be consulted as to the best conditions for maximizing the formation of the various stable oxides of phosphorus.

The reaction of phosphorus vapor with water vapor at high temperatures and pressures has been studied by several authors who were primarily

[18] F. S. Dainton and H. M. Kimberly, *Trans. Faraday Soc.*, **46**, 629 (1950).

interested in the over-all reaction and its products rather than in the mechanism of the rate process.[19] The following partial reactions are found:

$$P_4 + 6\,H_2O \longrightarrow 2\,HPO(OH)_2 + 2\,PH_3 \quad (4\text{-}13)$$

$$HPO(OH)_2 + H_2O \longrightarrow OP(OH)_3 + H_2 \quad (4\text{-}14)$$

$$PH_3 + 4\,H_2O \longrightarrow OP(OH)_3 + 4\,H_2 \quad (4\text{-}15)$$

When the over-all reaction is allowed to run to completion, only phosphoric acids and hydrogen are found. Naturally, if there is not sufficient water to give orthophosphoric acid, as shown in equations 4-14 and 4-15 above, condensed phosphoric acids should form. In the absence of catalysts, temperatures above 280°C. are essential for the oxidation of phosphorus by water. Under these conditions, reaction 4-13 for the formation of phosphorous acid is the most rapid. Catalysts—including salts of the transition metals, such as nickel and iron, and solvents for phosphorus—accelerate the oxidation of the phosphorus. The transition metals usually end up as phosphates. Phosphoric acid also seems to act catalytically, since the rate of oxidation of the phosphorus accelerates as this product is formed.

Normally, phosphorus vapor does not react with hydrogen gas. However, under pressure at 360°C., a mixture of phosphorus and hydrogen gave phosphine.[20] As would be expected, atomic hydrogen readily converts phosphorus into phosphine.[21] Phosphorus vapor reacts readily with halogens and sulfur in the vapor form. Carbon monoxide neither oxidizes phosphorus nor reduces its oxides, whereas carbon dioxide will oxidize phosphorus at temperatures above 650°C. A partial study of the equilibria in the P—C—O system has been carried out.[22] It is interesting to note that in mixtures of phosphorus vapor and carbon monoxide, the phosphorus can be preferentially oxidized by air without concomitant formation of an appreciable amount of carbon dioxide.

Phosphorus vapor is very poisonous[23] and care should be taken not to breathe it or expose the skin, through which the vapor can be absorbed.

[19] S. Brunauer and J. F. Schultz, *Ind. Eng. Chem.*, **33**, 828 (1941); V. N. Ipatiev and C. Freitag, *Z. anorg. u. allgem. Chem.*, **215**, 388 (1933); L. Hackspill, *Chim. & ind (Paris)*, **25**, 1058 (1931); J. Zawadzki and T. Borucki, *Przemysl Chem.*, **15**, 76 (1931). Also see C. Kroger, *Z. anorg. u. allgem. Chem.*, **206**, 289 (1932).

[20] V. Ipatieff and V. Nikolaieff, *Ber.*, **59B**, 595 (1926); V. Ipatieff, *ibid.*, **59B**, 1412 (1926)

[21] I. Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912).

[22] P. H. Emmett and J. F. Shultz, *Ind. Eng. Chem.*, **31**, 105 (1939), G. L. Frear, E. F. Ogg, and L. H. Hull, *ibid.*, **36**, 927 (1944).

[23] H. Heimann, *J. Ind. Hyg. Toxicol.*, **28**, 142 (1946).

Liquid Phosphorus

It is believed[15] that the same liquid is obtained no matter whether white, red, or black phosphorus is melted or the vapor is condensed. The vapor pressure curves of liquid white and liquid red phosphorus appear to be different sections of the same line; and, moreover, black and red phosphorus

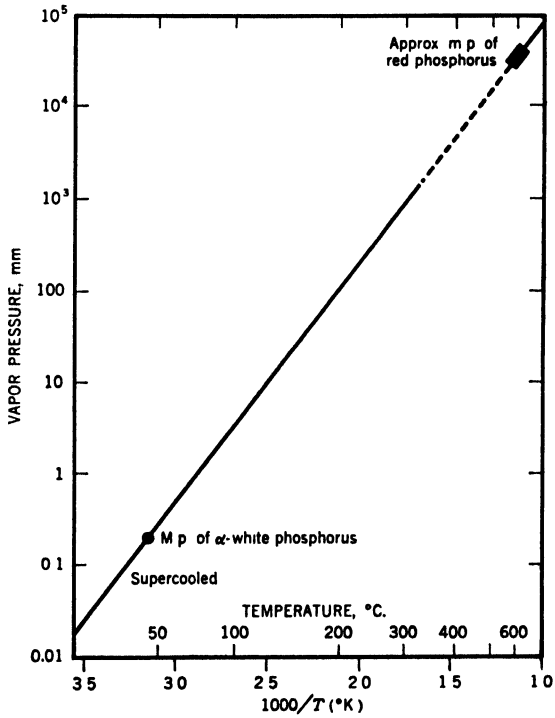


Fig. 4-4. Vapor pressure of liquid phosphorus. Because of the rapid formation of red phosphorus, the liquid does not exist in the region represented by the broken portion of the line.

melt to a common liquid[24] that yields white phosphorus on rapid cooling.

The vapor pressure[15] of liquid phosphorus is shown in Figure 4-4. Because of the rapid formation of red phosphorus, the liquid does not exist in the region represented by the broken portion of the line in Figure 4-4.

[24] P. W. Bridgman, *J. Am. Chem. Soc.*, **36**, 1344 (1914); W. Marckwald and K. Helmholtz, *Z. anorg. u. allgem. Chem.*, **124**, 81 (1922).

Values for the vapor pressure between 45° and 350°C. are given by the following equation

$$\log p_{\text{mm.}} = 18.8192 + (1.074 \times 10^{3})\,T - 3.906 \log T - (3.2167 \times 10^{3})/T \quad (4\text{-}16)$$

Liquid phosphorus, as usually prepared by melting commercial white phosphorus, is a straw-colored liquid which may have a small amount of colloidal red phosphorus dispersed in it so as to give the liquid a reddish tinge. Unpurified liquid phosphorus may occasionally also have a murky appearance, due to insoluble material, primarily oxides and oxyacids of phosphorus, which tend to collect on the surface. A simple method of purifying liquid phosphorus is to allow it to stand for several days at room temperature under a dilute aqueous solution of sulfuric acid and potassium dichromate. The phosphorus should then be washed with distilled water. Finally, additional purification can be obtained by distilling the phosphorus and collecting only the middle fractions.

Liquid phosphorus is very easily supercooled, and drops of 1 mm. diameter or less have been cooled[25] to −71.3°C., which is 115.6°C. below the melting point of white phosphorus! The crystallization of supercooled phosphorus is extremely rapid[26]—about 500 times faster than has been reported for other substances studied. At 25°C., the linear velocity of crystallization is 160 cm./sec.

The structure of liquid phosphorus has been studied by x-ray diffraction.[27] Radial density distribution curves resulting from this study are shown in Figure 4-5 for two temperatures, 48°C. and 226°C. These curves show three peaks: one at 2.25 A., the second at 3.9 A., and the third at 5.9 A. The area of the first peak is equivalent to 2.9 atoms, which means that each phosphorus has three nearest neighbors at 2.25 A. These three neighboring phosphorus atoms are permanently affixed to the atom in question, since the first peak is seen to extend down to the zero axis on both sides; and, furthermore, the shape and size of the peak are not affected by temperature. From the symmetrical shape of the first peak, it may be inferred that all phosphorus atoms are equivalent or very nearly so. These results strongly support the idea that the phosphorus atoms are present in liquid phosphorus in the form of symmetrical P_4 tetrahedra.

[25] J. H. Hildebrand and G. J. Rotariu, *J. Am. Chem. Soc.*, **73**, 2524 (1951).

[26] R. E. Powell, T. S. Gilman, and J. H. Hildebrand, *J. Am. Chem. Soc.*, **73**, 2525 (1951).

[27] C. D. Thomas and N. S. Gingrich, *J. Chem. Phys.*, **6**, 659 (1938).

The second peak in the radial density distribution pattern occurs at 3.9 A. and corresponds to the nearest approach of phosphorus atoms which are not in the same P_4 tetrahedron. The area of the peak indicates that there are some six to eight of such nearest neighbor atoms around each phosphorus atom. The third peak in the pattern occurs at 5.9 A. at 48°C. and at 6.1 A. at 226°C. This change with temperature is in accord with the coefficient of expansion. This third peak represents the 32–33 second nearest

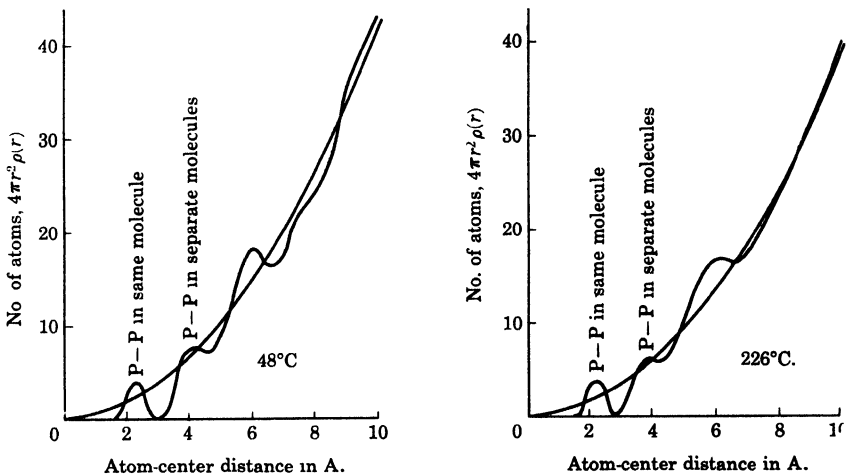


Fig. 4-5. Radial distribution curves from x-ray study of liquid phosphorus.[27]

neighboring atoms which are not in the same tetrahedron as the given phosphorus atom to which the radial distribution refers.

The Raman spectrum[28] of liquid phosphorus exhibits the three lines corresponding to the fundamental frequencies for a tetratomic tetrahedral molecule having T_d symmetry.

The density[29] and viscosity[30] of pure liquid phosphorus are given by the following equations, where d stands for the density in grams per cubic centimeter (g./cm.^{3}), η is the viscosity in centipoises, with t representing the temperature in °C.

[28] C. S. Venkateswaran, *Proc. Indian Acad. Sci.*, **2A**, 260 (1935); *ibid.*, **4A**, 345 (1936).

[29] S. Dobinsky, *Bull. intern. acad. polon. sci. Classe sci. math. nat.*, **1935A**, 253 (1935); G. Pisati and G. de Franchis, *Gazz. chim. ital.*, **4**, 497 (1874).

[30] A. N. Campbell and S. Katz, *J. Am. Chem. Soc.*, **57**, 2051 (1935); S. Dobinsky, *Bull. inter. acad. polon. sci. Classe sci. math. nat.*, **1934A**, 103 (1934).

$$d = 1.7862 - (9.195 \times 10^{-4})t \quad \text{for } 280°\text{C.} > t > 10°\text{C.} \quad (4\text{-}17)$$

$$\log \eta = -1.3879 + 514.4/(273.2 + t) \quad \text{for } 140°\text{C.} > t > 20°\text{C.} \quad (4\text{-}18)$$

When the liquid phosphorus is saturated with water, both the density and viscosity are affected. Thus at 50°C., a temperature somewhat above the melting point of white phosphorus, the density of liquid phosphorus is lowered from 1.740 to 1.737 g./cm.^{3} upon being saturated with water. Likewise, at the same temperature, the viscosity is lowered from 1.694 to 0.967 centipoises upon being saturated with water. The variations of the density and viscosity of liquid phosphorus saturated with water[31] are given by the following equations.

$$d = 1.782 - (9.0 \times 10^{-4})\, t \quad \text{for } 95°\text{C.} > t > 45°\text{C.} \quad (4\text{-}19)$$

$$\eta = 3.314 - (9.65 \times 10^{-2})\, t + (1.279 \times 10^{-3})t^2 - (5.76 \times 10^{-6})\, t^3 \quad \text{for } 95°\text{C.} > t > 45°\text{C.} \quad (4\text{-}20)$$

Liquid phosphorus boils at 280.5°C. at atmospheric pressure, and the critical temperature and pressure of liquid phosphorus are 695°C. and 82.2 atm.[32] Because of the rapid rate of formation of red phosphorus from the liquid in the temperature range from about 350 to 510°C., liquid phosphorus has not been observed in this range, although it can be obtained at higher temperatures. The electrical conductivity of liquid phosphorus at 25°C. is 4×10^{-7} mhos/cm.—a value quite near that for the alcohols and for water. The dielectric constant, however, is more similar to that of benzene, as would be expected. Its value at 45°C. is 3.85.

The solubility of water[33] in liquid phosphorus is 3.6 mg. H_2O/g. P_4 in the temperature range of 25–45°C. Mercury is also surprisingly soluble[34] in liquid phosphorus, with 0.29 mg. Hg/g. P_4 being dissolved at 25°C. This is the only known instance of a metal dissolving by a purely physical process in a nonmetallic liquid. This occurs because mercury has unusually low internal forces for a metal and phosphorus has higher internal forces than any known nonpolar, nonmetallic liquid. Their solubility parameters, δ (square root of the energy of vaporization per cubic centimeter), are 30.7

[31] N. D. Litvinov and I. E. Furmer, *J. Appl. Chem.* (*U.S.S.R.*), **7**, 321 (1934).

[32] A. Smits and S. C. Bokhorst, *Proc. Akad. Wetenschap.*, **18**, 106 (1915).

[33] G. J. Rotariu, E. W. Haycock, and J. H. Hildebrand, *J. Am. Chem. Soc.*, **74**, 3165 (1952).

[34] G. J. Rotariu, E. Schramke, T. S. Gilman, and J. H. Hildebrand, *J. Am. Chem. Soc.*, **73**, 2527 (1951).

TABLE 4-1
Allotropic Modifications of Phosphorus

Modification	Crystal structure	Density (g./cm.^{3})	Melting point (°C)	Heat of sublimation (kcal./mole)	Remarks
α-White	Cubic (a = 18.5 A.)	1 828	44 1	13 4	Atomic arrangement known: P_4 structure.
β-White	Orthorhomic or monoclinic?? Birefringent	1 88	—	—	Transforms to α-white on heating to −76.9°C.
Red I	Amorphous particles	2 16±	—	19 7	Transforms to II at 460°C.
Red II (?)	Hexagonal? Poorly crystalline	2 31	—	24	Transforms to III at 520°C.
Red III (?)	Hexagonal? Poorly crystalline	2 31	—	—	Transforms to IV at 540°C.
Red IV	Tetragonal (or less probably hexagonal)	2 31	—	28	Good x-ray powder pattern. More lines than II and III which may be poorly crystallized Form IV.
Red V	Triclinic	2 31	590	28 8	Many lines in x-ray powder pattern. Different from IV.
Red VI	? (Deep red color)	?	—	—	Made at 300°C. and 8000 atm. Different x-ray pattern than other forms of red phosphorus.
Brown	?	?	—	Decomp.	Made from hot P vapor by condensing on liquid-nitrogen cold-finger. Reverts to 20% red and 80% white P at temps. above ca. −150°C.
Amorphous black	Amorphous	2 25	—	—	Transition form in prep. of cryst. black P under pressure.
Black	Orthorhombic (a = 3.31, b = 4.38, and c = 10.50 A.)	2 69	—	30 5	Made by compressing to 12,000 kg./cm.^{2} at 200°C. Atomic arrangement known: infinite sheet structure.

for Hg and 14.5 for P_4, as compared with 24.5 for H_2O. When supercooled phosphorus saturated with mercury is allowed to crystallize, it becomes grey-black due to the separation of the mercury as fine globules. When mercury-saturated phosphorus is dissolved in carbon disulfide, the mercury is left behind in its usual metallic form.

Several multiple liquid phase systems which include phosphorus have been described.[35] In one of them eight liquid phases are in stable equilibrium with each other at 45°C. The phases, from top to bottom, are as follows: paraffin oil/silicone oil/water/aniline/perfluorodimethylcyclohexane/liquid phosphorus/gallium/mercury. The mutual insolubility of these liquids has been explained by Hildebrand in terms of differences in the kinds and relative strengths of the intermolecular force fields.

Allotropy of Solid Phosphorus

Many of the early workers in the field of phosphorus chemistry noticed that a reddish-colored substance often appeared along with ordinary phosphorus. This was usually attributed to the formation of a lower oxide, but it was not until the decade starting with 1840 that it was clearly understood that the red substance was an allotropic modification of phosphorus.[36] The third major modification, black phosphorus, was discovered by Bridgman in 1914.[37] Black phosphorus is formed at 200°C. under a high pressure of 12,500 kg./cm.^{2}.

Each of these major allotropic modifications of phosphorus exhibits more than one variety. Thus, there are two crystalline forms of white phosphorus, several varieties of red phosphorus, and two varieties of black phosphorus. A listing of the various varieties of elemental phosphorus is given in Table 4-1.

WHITE PHOSPHORUS

White phosphorus is the commonest form of this element, since it is the form that is obtained by condensing the vapor to a liquid and then allowing it to solidify. Commercial white phosphorus is a rather pure product, with the major impurities being arsenic (usually under 200 p.p.m.) and traces

[35] S. L. Kittsley and H. A. Goeden, *J. Am. Chem. Soc.*, **72**, 4841 (1950); J. H. Hildebrand, *J. Phys. & Colloid Chem.*, **53**, 944 (1949).

[36] M. Kohn, *J. Chem. Educ.*, **21**, 522, 524 (1944) relates the discovery of red phosphorus in 1847 by A. Schrötter. A few years before Schrötter, J. J. Berzelius and H. A. von Vogel postulated that the red material was a form of phosphorus, but Schrötter was the first to demonstrate this contention adequately. See A. Schrotter, *Sitzber. Akad. Wien*, **1**, 25, 310 (1848); *ibid.*, **2**, 301 (1849); *ibid.*, **8**, 241 (1852); *ibid.*, **9**, 414 (1852).

[37] P. W. Bridgman, *J. Am. Chem. Soc.*, **36**, 1344 (1914); *ibid.*, **38**, 609 (1916).

of oils (hydrocarbons). The name yellow phosphorus has often been given to this variety of the element because most preparations, as exemplified by the phosphorus of commerce, exhibit a yellowish coloration. Extremely pure white phosphorus, however, is either colorless or white in appearance, depending on the size of the crystals in the mass. It is a waxy material somewhat similar in appearance and texture to paraffin. White phosphorus is the most reactive solid form of elemental phosphorus. It burns in air but can be stored under water, with which it does not react under normal conditions. White phosphorus as solid or liquid is extremely poisonous when ingested, and care must be taken in handling it.

Two varieties of white phosphorus exist. The high-temperature variety, called α-white phosphorus, converts to the low-temperature form[37] at $-76.9°$C. at a pressure of 1 atm. The transition temperature is raised to $+64.4°$C. at 11,600 atm. The existence of two forms of white phosphorus has been demonstrated by x-ray studies[38] and by the fact that the β-variety is birefringent.[39]

The structure of the α-form of white phosphorus has been determined[38,40] by x-ray diffraction. α-White phosphorus is cubic with an extremely large unit cell containing 56 molecules of P_4. A radial density distribution curve shows a first peak at 2.3 A., with an area corresponding to approximately three neighboring atoms. This result is in accord with the existence of P_4 molecules and is consistent with the data obtained on gaseous and liquid phosphorus. In addition, the Raman spectrum[41] of solid α-white phosphorus and of a solution of α-white phosphorus in carbon disulfide is virtually identical with that of the liquid and the undissociated vapor. Because of this and because of the fact that simple crystallization of liquid phosphorus at reasonably low temperatures always gives α-white phosphorus, its appears quite certain that white phosphorus is made up of molecules consisting of a tetrahedron of phosphorus atoms, as shown in Figure 4-2.

There is considerable evidence that the P_4 tetrahedra in α-white phosphorus are free to rotate. This probably means that the transition from the α-variety to the β-variety of white phosphorus corresponds to a loss of this rotational freedom. The free rotation of the P_4 molecules in the solid is in

[38] T. Sugaware, Y. Sakamoto, and E. Kanda, *Sci. Repts. Research Insts. Tohoku Unw.*, **Ser. A 1**, No. 1, 29 (1949); T. Sugawara and E. Kanda, *ibid.*, **1**, 153 (1949); G. Natta and L. Passerini, *Atti accad. naz. Lincei, Mem., Classe sci. fis., mat. e nat.*, **24**, 464 (1936); *Nature*, **125**, 707 (1930).

[39] D. Vorlander, W. Selke, and G. Kreiss, *Ber.*, **58**, 1802 (1925).

[40] D. E. C. Corbridge and E. J. Lowe, *Nature*, **170**, 629 (1952).

[41] H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950); C. S. Venkateswaran, *Proc. Indian Acad. Sci.*, **2A**, 260 (1935); *ibid.*, **4A**, 345 (1936).

accord[25] with the loss in entropy on freezing of 1.984 e.u., which is exactly the value of the gas constant, R. Furthermore, nuclear magnetic resonance can be observed[42] in solid α-white phosphorus, using a high-resolution spectrometer. Usually with such an instrument, the presence of a resonance peak is observed only in liquids and gases and not in solids. The fact that

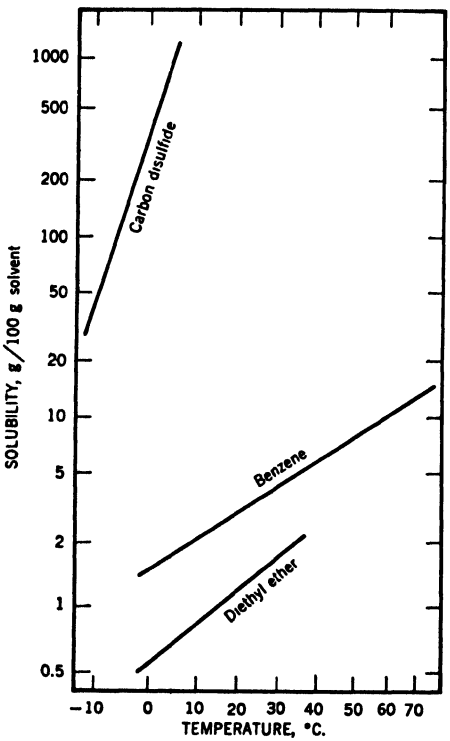


Fig. 4-6. Solubility of α-white phosphorus in three organic solvents. (The temperature is shown on a scale corresponding to the reciprocal of its absolute value.)

it is found in white phosphorus indicates that the P_4 molecules are free to undergo some type of thermal motion which is not coupled with the lattice vibrations. Presumably, the free rotation of the P_4 molecules in the crystal explains why the rate of crystallization of liquid phosphorus to form α-white phosphorus is so unusually rapid. The individual P_4 molecules do

[42] H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954); J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

not have to assume a certain angular arrangement in the crystal lattice, but, rather, pack together like spheres.

The sublimation pressure[43] of solid α-white phosphorus is given by the following equation,[15] which agrees very closely with experiment and is consistent with spectral, calorimetric, and vapor pressure data for the three states of elemental phosphorus.

$$\log p_{\text{mm}} = 1.9198 - (3.084 \times 10^{-3})\,T + 2.7763 \log T - (2.641 \times 10^{3})/T - (3.258 \times 10^{4})/T^{2} \quad (4\text{-}21)$$

According to this equation, the sublimation pressure of white phosphorus is 0.043 mm. at 25°C.

The best of the common solvents for α-white phosphorus is carbon disulfide, but liquid ammonia and liquid sulfur dioxide are also good solvents. A plot of the solubility[44] of α-white phosphorus in carbon disulfide, benzene, and diethyl ether is given in Figure 4-6. α-White phosphorus is considerably less soluble in water[45] (0.00033%) than in mineral oil (1.45%) at room temperature.

Reactions of White Phosphorus

In general, white phosphorus is considerably more reactive than the red variety, which, in turn, is somewhat more reactive than black phosphorus. This high reactivity is attributable to the strain introduced by the bent bonds in the P_4 molecule.[46] As in the case of phosphorus vapor, the reaction of solid white phosphorus with air or oxygen has been quite extensively investigated, and the phenomenon has been shown to involve a branching chain mechanism. Early investigators found many anomalies in the oxidation of white phosphorus.[47] These are briefly reviewed by Mellor. Oxygen at subatmospheric pressures or compressed air causes white phosphorus to emit a greenish glow which can be made to appear downstream from the phosphorus when the gas is blown over it. In addition to glowing.

[43] M. Centnerszwer, *Z. physik. Chem.*, **85**, 99 (1913); F. S. Dainton and H. M. Kimberley, *Trans. Faraday Soc.*, **46**, 912 (1950). Also see D. MacRae and C. C. Van Voorhis, *J. Am. Chem. Soc.*, **43**, 547 (1921).

[44] A. Seidell, *Solubilities of Inorganic and Organic Compounds*, 2nd ed., D. Van Nostrand Co., Inc., New York, 1919, p. 488. The technique of preparing solutions of phosphorus in carbon disulfide is given by S. Heilveil, *J. Chem. Educ.*, **30**, 305 (1953).

[45] C. Stich, *Pharmazie*, **8**, 202 (1953).

[46] Yu. V. Khodakov, *Doklady Akad. Nauk S.S.S.R.*, **42**, 125 (1944); also in English in *Compt. rend. acad. sci. U.R.S.S.*, **42**, 120 (1944).

[47] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longman's Green & Co., London, 1940, Vol. VIII, pp. 771-82.

white phosphorus may also oxidize very rapidly and burn with a bright yellow flame which may extend for a considerable distance from the phosphorus surface from which it proceeds. The intense reaction, which is accompanied by a flame, does not proceed at all when the pressure either exceeds a definite upper limit or else drops below a corresponding lower limit. These upper and lower limits are similar to the critical pressures described for the oxidation of phosphorus vapor.

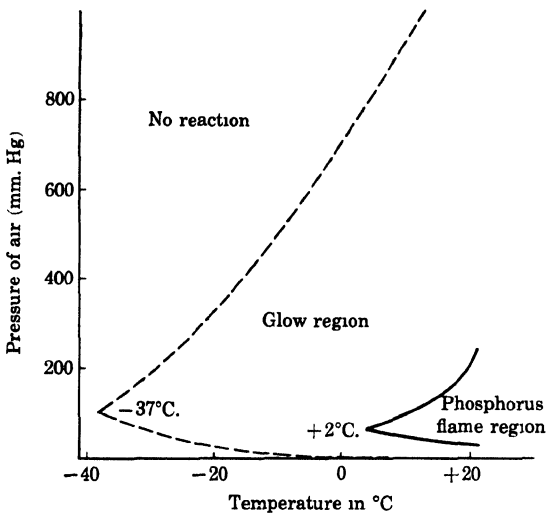


Fig 4-7. The effect of temperature on the flame and glow limits in the oxidation of solid white phosphorus by dry air.[48]

In a modern study[48] of the oxidation of α-white phosphorus, it was shown that there is also a definite boundary between the glow region and the flame region in the oxidation of phosphorus. The variations of these regions with the partial pressure of air and temperature are shown in Figure 4-7. As predicted by the branching-chain theory, hydrocarbons should have a considerable effect on the glow and flame boundaries, and an example of the kind of data obtained with α-white phosphorus in the presence of air and hydrocarbon vapors is shown in Figure 4-8. As the temperature is lowered, the flame region becomes greatly reduced, and the region of no reaction moves toward the left in Figure 4-8. The reverse is true when the

[48] F. S. Dainton and J. C. Bevington, *Trans. Faraday Soc.*, **42**, 377 (1946).

temperature is raised, with a considerable change in the diagram occurring with an increase or decrease of 10°C. in the temperature.

The greenish glow observed in the cold oxidation of phosphorus has been studied by a number of authors,[49] some of whom have shown considerable ingenuity in obtaining the spectrum of the glow. The spectrum shows a continuum in the visible region and a series of bands and lines stretching from 3418 to 2371 A. It is found that the same spectrum is obtained when

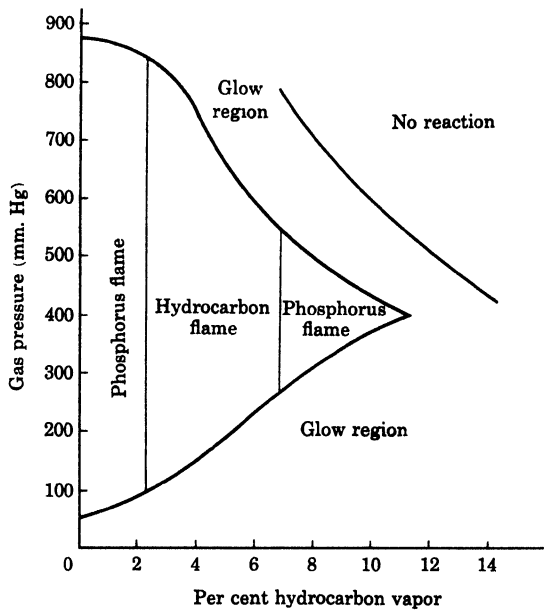


Fig. 4-8. The effect of hydrocarbons on the flame and glow boundaries in the air oxidation of solid white phosphorus at 44.5°C.[48]

P_2O_3 burns in moist air, so that the same excited constituents must be present in both cool flames. Some of the bands in these two spectra have been shown to be emitted by the unstable molecule PO.[50]

Under most conditions, the main product of the reaction between phosphorus and gaseous oxygen is phosphorus pentoxide, although the tetroxide,

[49] See A. Petrikaln, *Z. Physik*, **51**, 395 (1928), *Naturwiss.*, **16**, 205 (1928); W. Busse, *Ann. Physik*, **82**, 873 (1926); *ibid.*, **83**, 80 (1927). Also H. J. Emeléus and W. E. Downey, *J. Chem. Soc.*, **125**, 2491 (1924); H. J. Emeléus and R. H. Purcell, *ibid.*, **1927**, 788; E. J. Bowen and E. G. Pells, *ibid.*, **1927**, 1096.

[50] K. Rumpf, *Z. physik. Chem.*, **B38**, 469 (1938).

trioxide, and perhaps lower oxides, can also be produced in appreciable amounts under the proper conditions.[51]

Oxidizing agents other than oxygen also readily react with liquid and solid white phosphorus. Thus, the halogens, sulfur, and the various oxidizing acids give phosphorus halides, phosphorus sulfides, and the oxyacids of phosphorus, respectively. White phosphorus also reacts readily with a number of metals. These reactions will be discussed later in this chapter in the sections dealing with the metal phosphides.

White phosphorus is oxidized by aqueous solutions of the salts of metals, such as silver, which have a low redox potential. The reaction with solutions of copper sulfate form the basis of a safety measure used in industrial plants where elemental phosphorus is handled. Tubs of copper sulfate solution are placed in convenient locations so that persons contaminated with phosphorus can immerse themselves in the solution. The reaction between phosphorus and the copper sulfate solution proceeds gently; the phosphorus becomes coated with a black copper phosphide, which slowly forms crystalline copper, and soluble oxyacids of phosphorus are produced.[52] The black coating on the phosphorus prevents its burning in air. When elemental phosphorus is heated with aqueous solutions of strong alkalies, phosphine, PH_3, is formed.

It should be noted that white phosphorus is very poisonous when ingested.[53] As previously noted, the vapor is also toxic.

Conversion of White to Red Phosphorus

White phosphorus changes to amorphous red phosphorus when heated in a closed system at moderately high temperatures. During the early part of the conversion process, the reaction mixtures consist of particles of red phosphorus suspended in white phosphorus. When approximately half of the white phosphorus has been converted to the red variety, the mixture becomes semifluid; further conversion yields a solid product.[54]

The rate of conversion of liquid white phosphorus to red phosphorus follows a first-order reaction rate in the temperature range of 250–350°C. The activation energy of the process is about 38 kcal./mole, and the frequency factor has a normal value of 4×10^{12}. It appears that the P_4 molecule is not dissociated during the conversion process, and that exten-

[51] C. C. Miller, *J. Chem. Soc.*, **1929**, 1829.

[52] H. Pelabon, *Bull. soc. chim.*, **53**, 260 (1933), says that the phosphide has a Cu/P mole ratio of 5.6 and that the H_3PO_4/H_3PO_3 mole ratio is 5 for 0.1 *N* $CuSO_4$.

[53] R. S. Diaz-Rivera, P. J. Collazo, E. R. Pons, and M. V. Torregrosa, *Medicine*, **29**, 269 (1950)

sive chain reactions are not involved.[54] The conversion probably consists of a first-order production of nuclei of red phosphorus, followed by agglomeration of the nuclei to form larger particles. The process whereby the red phosphorus nucleates probably consists of a rearrangement of bonds between neighboring P_4 molecules to give the structure of red phosphorus.

Addition of 0.01–0.1% of iodine or of 0.5–1.5% sulfur to liquid white phosphorus markedly accelerates the initial stages of the conversion to red phosphorus. This accelerating effect soon disappears, however, and the conversion then continues at a rate comparable to that found when no accelerators are present. De Witt and Skolnick conclude that catalysis of the conversion process sets up a chain reaction which is independent of temperature, and that an atom of iodine is about forty times as effective as an atom of sulfur. Apparently, the iodine and sulfur atoms are built into the structure of the red phosphorus as it forms, so that they are thus removed from the reaction zone. It is interesting to note that the average particle size of the red phosphorus increases as the reaction whereby it is formed from liquid white phosphorus proceeds.[55] At 400°C. the white phosphorus is essentially all converted to the red form in 1 hr. 30 min.

Ultraviolet radiation also accelerates the conversion of α-white phosphorus to amorphous red phosphorus. Thus, it is generally desirable to store purified white phosphorus in the dark. When bricks of white phosphorus under water are exposed to light for a considerable length of time, nodules of red phosphorus are found to encrust the surface. Occasionally at one or two points on the surface, large nodules of red phosphorus form with none occurring elsewhere on the surface.

The conversion of white phosphorus dissolved in PBr_3 to red phosphorus, which forms as a precipitate, has been measured[56] and found to be a first-order reaction with an activation energy of about 4.5 kcals./mole. The rate constant is 7.8×10^{-3} min.$^{-1}$ at 184°C. This reaction is accelerated by light, and the photochemical aspects of the conversion in carbon disulfide have been studied.[57] When white phosphorus is dissolved in this solvent, the rate of precipitation of red phosphorus is also found to be a first-order process. It was concluded that the photochemical reaction consists in a dissociation of the P_4 molecules into P_2 molecules which, in turn, recombine to form red phosphorus.

[54] T. W. De Witt and S. Skolnik, *J. Am. Chem. Soc.*, **68**, 2305 (1946). Also see A. A. Vvedenskii and A. V. Frost, *J. Gen. Chem.* (*U.S.S.R.*), **1**, 917 (1931); A. Ya. Zvorykin, *J. Appl. Chem.* (*U.S.S.R.*), **9**, 779 (1936).

[55] S. Skolnik, G. Tarbutton, and W. E. Bergman, *J. Am. Chem. Soc.*, **68**, 2310 (1946).

[56] R. Schenck, *Ber.*, **36**, 979, 4202 (1903); *Z. Elektrochem.*, **11**, 117 (1905).

[57] G. Rathenau, *Physica*, **4**, 503 (1937).

RED PHOSPHORUS

There are many conflicting reports in the literature on the structure and properties of red phosphorus. Red phosphorus prepared by various methods exhibits different properties. Measured densities have been found to vary between 2.0 and 2.4 g./cm.^{3}, and the melting points range from 585 to 600°C The sublimation pressure has also been found to depend on the exact preparation. And the color of red phosphorus is found to vary from a deep scarlet to brown, and to violet, depending on the method of preparation. In general, it appears that the large crystals of red phosphorus have a purplish color, whereas the most finely divided material is a bright scarlet red.[55]

Commercial red phosphorus is almost entirely amorphous, as are also laboratory preparations obtained by conversion of liquid white phosphorus below 350°C.[15] Red phosphorus prepared by deposition on a wall at 200–425°C. from phosphorus vapor in contact with a heated tungsten filament is also amorphous. Amorphous red phosphorus deposited from the vapor at pressures below 1 atm. appears under a microscope to be in the form of vitreous films. In addition, x-ray powder photographs show a broad, diffuse ring. The radial density distribution curve[27] for amorphous red phosphorus is somewhat similar to the curve for liquid phosphorus shown in Figure 4-5. The first peak at 2.29 A. corresponds to the three nearest neighbors. The second peak at 3.5 A. is interpreted as being due to the next nearest neighbors, of which there are on the average 6.7 per phosphorus atom. From these two distances, it appears that the P—P—P bond angle is equal to about 99° in amorphous red phosphorus. The third peak which appears in the radial density distribution curve of liquid P_4 (Fig. 4-4) does not show up in the radial density distribution curve for amorphous red phosphorus. This latter curve exhibits only the two pronounced maxima.

Because of the fact that catalysts[54,58] for conversion of white phosphorus to the red variety are taken up by the amorphous red phosphorus as it is formed, it is quite reasonable to assume that the atoms of the catalyst act as end groups on the molecules of red phosphorus, which can be conceived as large, rather randomly arranged arrays of phosphorus atoms, each one of which is bonded to three neighbors. Variations of this idea have occasionally appeared in the literature on red phosphorus, but the idea has been brought into focus by a recent paper by Kraft and Parini.[59] These authors explain the observed variety in the forms and properties of red phosphorus

[58] H. Krebs, *Z. anorg. u. allgem. Chem.*, **266**, 175 (1951).

[59] M. Ya. Kraft and V. P. Parini, *Doklady Akad. Nauk S.S.S.R.*, **77**, 57 (1951).

in terms of different degrees of polymerization and different terminal groups, which are always impurities. They point out that amorphous red phosphorus formed by irradiation in various solvents has incorporated within it small amounts of impurities derived from the solvent. In the case of organic halides as solvents, the organic radical appears to be strongly affixed to the phosphorus, since it cannot be removed by boiling with water, and oxidation of the phosphorus with nitric acid yields the corresponding alkyl or aryl phosphinic acids.

A thermal analysis of the process occurring when amorphous red phosphorus is heated shows three reproducible peaks,[60] with the first peak starting to form at 460°C., the second at about 520°C., and the third at about 540°C. as an additional hump on the second peak. All of these peaks corresponded to exothermic effects, with the first one being of the order of magnitude of 200 cal./gram-atom, and the other two being approximately one-third and one-fourth as large. Phosphorus corresponding to the areas between the peaks in the thermal analysis curve exhibited x-ray patterns of increasing complexity. The varieties of red phosphorus listed in Table 4-1 are related to the thermal analysis curve as follows: Red phosphorus-I is the original amorphous material, which transforms to red phosphorus-II at 460°C. The second transformation showing up in the thermal analysis curve corresponds to red phosphorus-II going to red phosphorus-III at 520°C., and the transformation from red phosphorus-III to red phosphorus-IV occurs at 540°C. The x-ray patterns of Forms-II and -III show only seven lines each, most of which are rather weak. However, the variety called Form-IV is well crystallized, in that thirteen lines are reported, of which five are of medium intensity. From the x-ray data, it is quite possible that Forms-II and -III are identical. And, in fact, Forms-II and -III may even be poorly crystallized varieties of Form-IV. Microscopic examination[15,60] of crystals grown from the vapor indicates that there are tetragonal and hexagonal forms of red phosphorus. Form-IV is probably the tetragonal variety, and Forms-II and/or -III (if they are different from Form-IV) may be hexagonal. It should be noted that the transitions found by thermal analysis are not reversible, since they only occur on heating. Following the amorphous polymer idea of Kraft and Parini, it is possible that these transitions correspond to cooperative changes in structure in which there is irreversible loss of end groups from amorphous or poorly crystallized red phosphorus.

Form-IV of red phosphorus is definitely well crystallized and exhibits

[60] W. L. Roth, T. W. DeWitt, and A. J. Smith, *J. Am. Chem. Soc.*, **69**, 2881 (1947).

birefringence ($n_\omega = 2.72$ and $n_\epsilon = 3.15 - 3.20$). It is produced as well-formed crystals by slow condensation of phosphorus vapor at 425°C. and a pressure of about 1 atm., or it can be made at 535°C. and a pressure of about 20 atm. on surfaces kept approximately 25°C. cooler than the vapor. It can also be made in a microcrystalline form by allowing molten phosphorus at about 600°C. to cool and then holding it at a temperature around 550°C. for crystallization.[61]

The crystalline modification of red phosphorus which has been best defined is the triclinic variety—denoted as Form-V in Table 4-1. This is prepared by slow condensation (up to 30 days) from the vapor at 550°C. on a surface maintained at 545°C. It also can be made by heating amorphous red phosphorus at 550°C. for several weeks. Differential thermal analysis shows no heat effects corresponding to the transition from red phosphorus-IV to red phosphorus-V.[60] The Form-V variety of red phosphorus probably represents the violet phosphorus, "metallic" phosphorus, or Hittorf's phosphorus of the early literature. The Hittorf[62] procedure for preparing this form of phosphorus is based on heating phosphorus in contact with lead at a temperature in the range of 500–600°C. The phosphorus dissolves in the lead and on cooling forms small, dark, reddish violet crystals which are separated from the lead by treatment with dilute nitric acid, which does not attack the phosphorus. The x-ray powder patterns given by Frost[61] for red phosphorus crystallized from lead at 525–590°C. and from bismuth at 570–580°C. correspond to the patterns obtained on the triclinic variety of red phosphorus by Roth, DeWitt, and Smith.[60]

It is interesting to note that a cubic form of red phosphorus has also been reported.[63] This material was made by heating ordinary red phosphorus at temperatures near 600°C. The unit cell of the crystal is large ($a_0 = 11.3$ A.), containing about 66 phosphorus atoms.

Red phosphorus has a low volatility as compared to white phosphorus. Thus, heating red phosphorus for 50 hr. at 100°C. under 0.5 mm. pressure showed no detectable amount of sublimation.[64] The sublimation pressures of the various forms of red phosphorus listed in Table 4-1 are given by the following equations in which p_{atm} stands for the pressure in atmospheres, and T is the absolute temperature.

For Form-I in the temperature range of 320–500°C.

[61] A. V. Frost, *J. Russ. Phys.-Chem. Soc.*, **62**, 2235 (1930).

[62] W. Hittorf, *Phil. Mag.*, **31**, 311 (1865); A. Stock and F. Gomolka, *Ger.*, **42**, 4511 (1909).

[63] G. E. Klein, *Am. Mineralogist*, **32**, 691 (1947).

[64] P. N. Raikov, *Z. anorg. u. allgem. Chem.*, **228**, 127 (1936).

$$\log p_{\text{atm.}} = -4296/T + 6.404 \tag{4-22}$$

For Form-II in the temperature range of 310–500°C.

$$\log p_{\text{atm}} = -5250/T + 7.61 \tag{4-23}$$

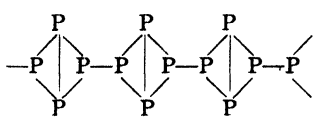
For Form-IV in the temperature range of 380–560°C.

$$\log p_{\text{atm}} = -6070/T + 8.67 \tag{4-24}$$

For Form-V in the temperature range of 320–510°C.

$$\log p_{\text{atm.}} = -6298/T + 8.944 \tag{4-25}$$

Measurement of the vapor pressure of red phosphorus by evaporation in a vacuum gives values for the vapor pressure which are about 10^{-7} times smaller than those obtained by normal static methods for determining vapor pressures. This has been explained by the hypothesis that P_2 molecules, rather than P_4 molecules, evaporate from red phosphorus.[65] According to this hypothesis, the vapor pressure in a static method of measurement is due almost completely to P_4 molecules; whereas, in a molecular distillation procedure, the P_2 molecules evaporating from the surface have no opportunity to combine to give P_4, so that the apparent vapor pressure is abnormally small. Support to this hypothesis is said to be given by experiments in which red phosphorus was evaporated in a high vacuum and condensed onto a cooled glass surface.[65] It was found that the condensate consisted of red phosphorus which may have formed because of the proposed close relationship between P_2 vapor and red phosphorus or because the energetic P_2 molecules were able to move around on the surface sufficiently so as to form amorphous red phosphorus which is simply more thermodynamically stable than is white phosphorus. Furthermore, a jet of P_2 vapor was found to deposit as red phosphorus on a cool glass surface, whereas P_4 vapor condensed to white phosphorus under the same conditions. Although the results in the last-mentioned experiment could be attributed to heating of the surface by the P_2 vapor, these experiments give some indication that red phosphorus may be some kind of a three-dimensional network in which pairs of phosphorus atoms can readily dissociate. Such a structure has been suggested by Pauling and Simonetta.[11] In this structure, it is postulated that there is the following type of molecular chains.



(4-26)

[65] H. W. Melville and S. C. Gray, *Trans. Faraday Soc.*, **32**, 271, 1026 (1935).

A random, cross-linked assemblage of such chains with atoms other than phosphorus in terminal positions would be in accord with the ideas of Kraft and Parini,[59] referred to previously on the structure of amorphous red phosphorus.

The deep-red form of phosphorus, denoted as Form-VI in Table 4-1, was made by A. F. Birch by subjecting white phosphorus to a pressure of 8000 atm. at 300°C. This variety of red phosphorus, which is only mentioned in the literature,[66] has a different x-ray pattern[67] than any of the five other forms of red phosphorus listed in Table 4-1.

A new form of phosphorus which apparently is somewhat related to red phosphorus was reported in 1953.[68] This form, called brown phosphorus, is obtained by condensing phosphorus vapor at 1000°C. or higher on a liquid-nitrogen-cooled surface. The brown phosphorus appears to be indefinitely stable at liquid-nitrogen temperatures (−196°C.); however, at temperatures greater than about −100°C., it changes irreversibly to a mixture of 20% red phosphorus and 80% white phosphorus. Measurements of the rate of conversion in the temperature range from −100 to −50°C. give an activation energy of about 3 kcal./mole for the change. Brown phosphorus may also be prepared by heating ordinary red phosphorus in an evacuated chamber at 350°C. or higher and condensing the vapor on a finger cooled with liquid nitrogen. White phosphorus at −190°C. exposed to the light from a quartz mercury lamp also gradually changes to the brown form. Further study of this brown phosphorus is surely needed.

Reaction of Red Phosphorus

Contrary to the usual impression, commercial red phosphorus is a moderately unstable material. At normal temperatures and humidities, red phosphorus reacts slowly with the water vapor and oxygen in air to form phosphine and a mixture of the oxyacids of phosphorus. This slow oxidation is exothermic and is accelerated by an increase in temperature, so that spontaneous combustion may result if large quantities of red phosphorus are stored in piles.

The rate of the reaction whereby red phosphorus is oxidized by moist air is accelerated appreciably by small concentrations of metals.[69] Copper,

[66] R. Hultgren, N. S. Gingrich, and B. E. Warren, *J. Chem. Phys.*, **3**, 351 (1935).

[67] B. E. Warren, private communication at the Mass. Inst. of Technol. to C. C. Stephenson.

[68] F. O. Rice, R. Potocki, and K. Gosselin, *J. Am. Chem. Soc.*, **75**, 2003 (1953).

[69] M. S. Silverstein, G. F. Nordblom, C. W. Dittrich, and J. J. Jakabcin, *Ind. Eng. Chem.*, **40**, 301 (1948).

bismuth, silver, iron, and nickel markedly increase the rate of oxidation; cadmium and tin increase the rate moderately; lead and chromium have little effect; whereas aluminum and zinc decrease the rate. Since iron and copper are usually present in commercial red phosphorus in concentrations of about 250 and 30 p.p.m., respectively, removal of these metals will noticeably increase the stability of the red phosphorus.[15] Moreover, addition of certain substances, such as hydrated aluminum oxide precipitated from solutions in the presence of the red phosphorus, is found to inhibit the oxidation.

BLACK PHOSPHORUS

There are two forms of black phosphorus: the crystalline variety of high density (2.69 g./cm.^{3}) originally described by Bridgman[37] and an amor-

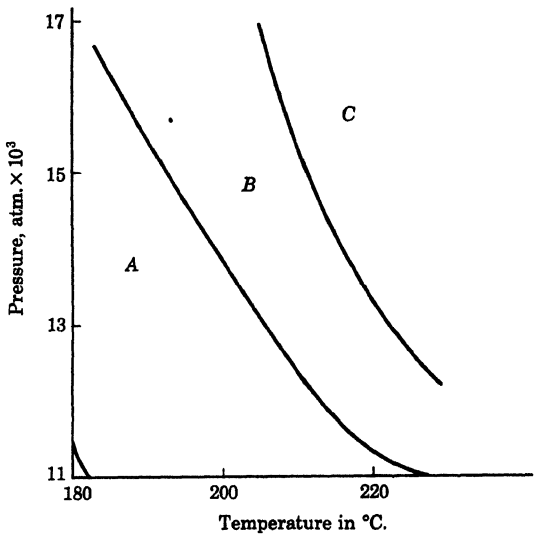


Fig. 4-9. Regions of temperature and pressure corresponding to the formation of black phosphorus.[70] *A* represents formation of amorphous black phosphorus. *B* represents formation of amorphous black phosphorus followed by transition to crystalline variety. *C* represents immediate formation of crystalline black phosphorus.

phous material[70] of intermediate density (2.25 g./cm.^{3}). The various regions of pressure and temperature in which the amorphous and crystalline forms of black phosphorus are found are shown in Figure 4-9. It should be

[70] R. B. Jacobs, *J. Chem. Phys.*, 5, 945 (1937).

noted that, at the highest temperatures and pressures, white phosphorus is practically instantaneously transformed to the black crystalline variety; whereas, at lower temperatures and pressures, the noncrystalline variety of black phosphorus is formed. In addition, there is an intermediate region where the amorphous variety forms first and then transforms to crystalline black phosphorus. In this region, there is an induction period of a few minutes in which there is a slow decrease in pressure at constant volume.

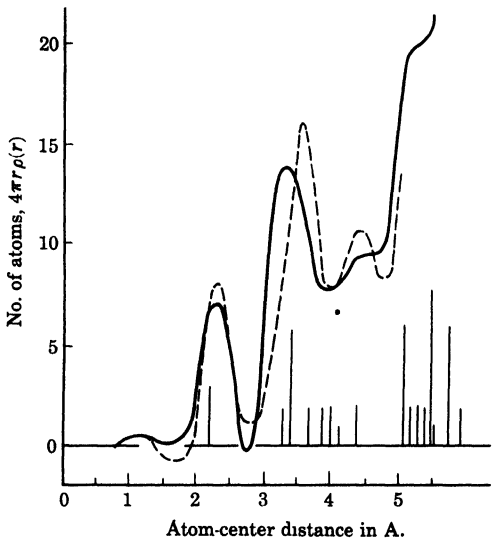


Fig. 4-10 Radial density distribution curves for black phosphorus.[27,65] The solid line represents values for the amorphous variety, and the dotted line stands for crystalline black phosphorus. The solid vertical lines indicate the number of atoms to be found for different planes in crystalline black phosphorus.

This is followed by an almost instantaneous drop in pressure when the amorphous black phosphorus converts to the crystalline variety.

Preparation of black phosphorus without the use of pressure has recently been reported.[71] In this procedure, equal weights of white phosphorus and of mercury are heated with a few seed crystals of black phosphorus at 370°C. for eight days. The mercury is removed from the product by heating it with metallic lead for several days at 300–450°C. If gold is used instead of lead as the mercury scavenger, a more pure form of black phosphorus results. The x-ray diffraction pattern and other

[71] H. Krebs, H. Weitz, and K. H. Worms, *Z. anorg. u. allgem. Chem*, **280**, 119 (1955)

physical properties aside from color give proof that black phosphorus and not simply white phosphorus blackened by mercury is formed by this procedure.

X-ray data[27,66] on the two forms of black phosphorus are interpreted in Figure 4-10 in terms of radial density distribution curves. The first peak for both the crystalline and the amorphous variety are very similar. In the amorphous variety, this first peak corresponds to three neighboring atoms at a distance of 2.27 A. Since the peak goes down to the axis on either side, the neighboring atoms are permanently affixed to the phosphorus atom in question. The second peak at 3.34 A. corresponds to next nearest neighbors. From these two atom-center distances, an average P—P—P angle of 95.6° can be calculated for amorphous black phosphorus.

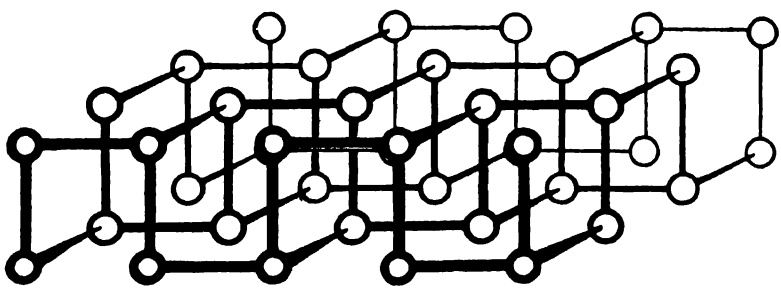


Fig. 4-11. The arrangement of atoms in the corrugated planes found in crystalline black phosphorus.

The only form of solid elemental phosphorus in which the atomic parameters have been unequivocably determined is the crystalline black variety. Crystals of this variety are orthorhombic and contain eight atoms in the unit cell. The crystal is composed of corrugated layers made up of phosphorus atoms, each bonded to three neighboring phosphorus atoms. In other words, the phosphorus atoms can be thought of as being in a layer made up of two halves separated by 2.28 A. A representation of this corrugated structure is shown in Figure 4-11. Each phosphorus atom exhibits two bond angles of 99° and one of 103°30′. The two 99° bond angles are in the plane of the layer, whereas the 103°30′ angle connects the layer halves. Thus, each corrugated layer consists of a giant molecule with adjacent layers being bound together less strongly than neighboring rows of atoms in the same layer. As might be expected, crystalline black phosphorus exhibits a flakiness somewhat similar to that of mica and graphite.

The sublimation pressure of black phosphorus has not been determined

TABLE 4-2

Recognized Binary Compounds of Phosphorus Arranged According to the Periodic Table
(High-temperature compounds not stable at room temperature are shown in brackets)

																H [HP] P_2H P_2H_4 PH_3	He Perhaps an interstitial compound
Li Li_3P_5 Li_3P	Be Be_3P_2											B BP B_4P_4	C [CP C_3P	N [PN PN P_3N_5	O [PO] P_4O_6 PO_2 P_4O_8 P_2O_5	F PF_3 PF_5	Ne None
Na Na_3P_5 Na_3P	Mg Mg_3P_2											Al AlP	Si SiP	P [P_4] black P red P P_4	S P_4S_3 P_2S_5 P_4S_7 P_4S_{10}	Cl PCl_3 PCl_5	A None
K K_3P_5	Ca Ca_3P_2	Sc Not investigated	Ti TiP_2 TiP $TiP_{0.95}$ Ti_3P	V VP_4 VP V_4P_3 V$_3$P V_2P	Cr CrP_4 CrP $CrP_{0.9}$ Cr_2P Cr_3P	Mn MnP_4 MnP Mn_3P_2 Mn_2P Mn_3P	Fe FeP_2 FeP Fe_4P Fe_3P	Co CoP_3 (?) Co_2P_3 (?) CoP $Co_2P_{1.2}$ (?) Co_2P Co_4P (?)	Ni NiP_3 Ni_2P_3 Ni_4P_3 Ni_2P Ni_3P_2 Ni_3P	Cu CuP_2 Cu_3P_2 (?) Cu_4P (?) Cu_3P	Zn ZnP_2 Zn_3P_2	Ga GaP	Ge GeP	As AsP	Se P_4Se_3 P_2Se_3	Br PBr_3 PBr_5	Kr None
Rb Rb_3P_5	Sr Sr_3P_2	Y Not investigated	Zr ZrP_2 ZrP $ZrP_{0.95}$ Zr_3P	Nb NbP_3 NbP $NbP_{0.95}$	Mo MoP_2 MoP Mo_3P	Tc Not investigated	Ru RuP_2 RuP Ru_2P	Rh RhP_3 RhP_2 Rh_3P_5 Rh_2P Rh_3P	Pd PdP_3 Pd_3P_2 Pd_7P Pd_3P	Ag AgP_3 AgP_2 Ag_3P	Cd CdP_2 Cd_3P_2	In InP	Sn SnP_3 Sn_3P_4 Sn_4P_3	Sb None (?)	Te Te_2P_2	I P_2I_4 PI_4	Xe None
Cs Cs_3P_5	Ba BaP_3 BaP_2 Ba_3P_4	La* LaP	Hf Not investigated	Ta TaP_2 TaP	W WP_2 WP W_2P W_4P	Re ReP_2 ReP_4 ReP Re_2P	Os OsP_2	Ir IrP_2 Ir_2P Ir_3P	Pt PtP_2 $Pt_{2.8}P$	Au Au_2P_3 Au_3P	Hg Hg_3P_2 (?)	Tl TlP_3 Tl_3P (?)	Pb Pb_3P_4 PbP_3 (?)	Bi None (?)	Po Not investigated	At Not investigated	Rn None
Fr Not investigated	Ra Not investigated	Ac** Not investigated															

*	Ce CeP	Pr PrP	Nd NdP	Pm Not investigated	Sm Not investigated	Eu Not investigated	Gd Not investigated	Tb Not investigated	Dy Not investigated	Ho Not investigated	Er Not investigated	Tm Not investigated	Yb Not investigated	Lu Not investigated
**	Th Th_3P_4 ThP	Pa Not investigated	U UP_2 U_3P_4 U_2P_3 (?) UP	Np Np_3P_4	Pu Not investigated	Am Not investigated	Cm Not investigated	Bk Not investigated	Cf Not investigated					

with great accuracy. However, it is given approximately by the following equation:

$$\log p_{mm} = -7560/T + 13.36 \qquad (4\text{-}27)$$

The electrical resistivity[72] of crystalline black phosphorus is considerably lower than that of the other forms of phosphorus but is still extremely high as compared to the metals. The electrical resistivity of black phosphorus is equal to 0.711 ohm-cm.[3] at 0°C. The resistivity decreases with pressure and temperature, with the temperature coefficient, $(1/R)(dR/dT)$, being equal to $-0.0077/°C$. Since the conductivity of the most metallic form of arsenic is about 2×10^4 times greater than that of phosphorus and the conductivity of graphite is about 500 times greater, black phosphorus should definitely not be considered as a semimetal. The comparison often made between black phosphorus and graphite (which has conducting electrons which can freely move in the direction of the cleavage planes of the crystal) is very misleading in that it implies that black phosphorus also has freely moving electrons, somewhat as in a metal. This is not true.

From a thermodynamic viewpoint, it appears that crystalline black phosphorus is the most stable form of this element.[73] However, α-white phosphorus is usually used as the standard comparison state in tables of thermodynamic data. Black phosphorus is the least reactive of the solid forms of elemental phosphorus. Indeed, it can be sawed and machined with safety and is completely stable in air. It can be ignited, but with difficulty, with a match.

THE PHOSPHIDES

Binary Compounds of Phosphorus

A listing is given in Table 4-2 of the relatively well-proven compounds in which phosphorus is combined with one other element. These binary compounds of phosphorus are of three major types: (1) simple molecules, which are readily volatilized; (2) complex polymers, in which the phosphorus atoms alternate with other atoms in a three-dimensional or planar network structure; (3) metalloid compounds, which range in properties from those of the so-called "hard metals" toward those of covalently bonded polymers. Some of the metal phosphides may also exhibit a considerable

[72] P. W. Bridgman, *Proc. Natl. Acad. Sci.*, **21**, 109 (1935).

[73] This is based on unpublished entropy measurements by C. C. Stephenson of the Mass. Inst. of Technol., Cambridge, Mass. See the Ph.D. Theses of R. L. Potter (1948), T. G. Maple (1949), and others.

amount of ionic character in their bonding so as to give salt-like properties to the compound.

Most of the binary compounds of phosphorus with the elements of Groups VIA and VIIA lie in the class of volatile molecular compounds. With respect to its compounds with phosphorus, hydrogen acts as if it were a member of Group VIIA and is not at all similar to the Group IA metals. The only known volatile molecular compound of phosphorus with an element in Group VA is the P_4 molecule (a phosphorus compound of phosphorus). Then there are the high-temperature molecules which show up in spectrographic investigations but are not stable at room temperature. Examples are found in the PH, PO, and PN molecules. These high-temperature molecules are all enclosed in square brackets in Table 4-2.

Most of the binary compounds of phosphorus with the elements of Groups IIIA, IVA, and VA can probably be considered as covalently bonded polymers. In addition, vitreous P_2O_5, the crystalline varieties of P_2O_5 exhibiting a low vapor pressure, and the solid hydrogen phosphide with the empirical formula P_2H exemplify the formation of polymers among the binary compounds of phosphorus with the elements of Groups VIA and VIIA. It should be noted that, generally speaking, binary compounds of phosphorus with the elements of Groups IIIA, IVA, VA, and VIA exhibit un-ionized molecular structures in which the atoms of both elements are covalently bonded to their neighboring atoms.

The term "hard metals" is used to describe a group of very hard substances with metallic character which have the following distinguishing properties: high hardness value, high melting point, good resistance to chemical attack, and high conductivity for heat and electricity. In general, it is found that the borides, carbides, silicides, nitrides, and phosphides—as well as some oxides and sulfides—of the transition metals constitute the class of hard metals.[74] The typical crystal structure of a hard metal consists of an arrangement of the transition-metal atoms often similar to that found in metals (close packing of spheres) with the carbon, nitrogen, phosphorus, or other modifying atoms filling the interstices between the transition-metal atoms. In the case of transition-metal phosphides for which the metal-to-phosphorus ratio (M/P) is equal to or greater than one, the phosphorus atom, which is large with respect to the boron and carbon atoms, causes an expansion of the metal lattice so that the distance between the centers of the transition-metal atoms is increased by about 15% over the distance found in the pure metals. The structure of the transition-metal phosphides for which $M/P < 1$ is not well understood as yet. As a class, however,

[74] G. Hägg, *Iva*, **24**, 343 (1953).

these phosphides appear to be somewhat similar to the lower phosphides in that they exhibit metal-like properties. Presumably, the transition-metal phosphides for which $M/P < 1$ are intermediate between the hard metals and the metalloid polymers—such as silicon, black phosphorus, and aluminum phosphide.

The binary compounds of phosphorus with the metals of Groups IA and IIA are usually described in the literature as being salt-like. Preparations made to date do not have a metallic appearance and, indeed, it is said that Mg_3P_2 is transparent. If phosphorus can exist as a negative ion, it will probably be in these compounds. However, there is no definite evidence available at present as to the amount of ionic character in the bonds between the alkali metal or alkaline earth metal atoms and the phosphorus atoms. Such data should be obtained. The question of the type of bonds existing in the binary compounds of the alkali or alkaline earth metals with boron, carbon, silicon, nitrogen, or phosphorus should be examined by the best modern techniques of structure analysis The alkali metals, in particular, are usually considered as being ionized in all of their compounds; whereas, carbon and phosphorus, for example, have been shown to be covalently bonded to their neighboring atoms in all cases in which the bond type has really been determined and not simply postulated, as is so often done. Which type of bonding prevails in the binary compounds? Presumably, there is a covalent bond with considerable ionic character. The binary compounds of phosphorus with the elements of Groups VIIA and VIA, as well as the phosphorus nitrides, are described in Chapters 5 and 6. The remaining binary compounds of phosphorus are described in this chapter.

As would naturally be expected, phosphorus does not form compounds with the noble gases. However, there is one report in the literature which indicates that helium is either strongly absorbed or forms an interstitial compound with elemental phosphorus at liquid-air temperatures.[75]

Historical and General Considerations of the Phosphides[76]

In the latter part of the Eighteenth Century, study of the metal phosphides was begun.[77] Since that time, a great deal of work has been done

[75] E. H. Boomer, *Nature*, **115**, 16 (1925).

[76] Much of the information given here and in the remainder of this chapter was obtained from R. C. Yalman, unpublished manuscript. Also see T. D. Farr, Phosphorus—Properties of the Element and Some of Its Compounds, *T.V.A. Chem. Eng. Rept. No.* 8, U S. Govt Printing Office, Washington, D. C , 1950.

[77] B. Pelletier, *Ann. Chim. Phys.* **1**, No. 1, 105 (1789); *ibid.*, **13**, 109, 132 (1792) [phosphides of precious metals, Pb, Mo, and Sb]; A. S. Marggraf, *Chem. Schrift. (Berlin)*, **1**, 42 (1762); B. G. Sage, *Mém. Acad.*, **1779**, 210 [copper phosphides].

TABLE 4-3
Some Typical Phosphides

Other element	Phosphide	Melting point (°C.)	Density (g / cm.)	Color and crystal system	Heat of formation from red P and the metal (kcal.)	Reaction with						
						Cold H_2O	Hot H_2O	Dilute acids	Dilute bases	Strong oxidizing acids	Strong bases	Alkaline melts
Aluminum	AlP	>1700	2 42	Grey-white, cubic		Mod.	Fast					
Arsenic	AsP			Black crystals		Mod.	Fast					
Beryllium	Be_3P_2		2 24	Brown, cubic		Fast	Fast					
Boron	BP			Maroon powder		No	No	No		Fast	Yes	Yes
Cadmium	CdP_2	ca. 700		Orange-red, pseudocubic		No	No	Slow				
	Cd_3P_2			Steel grey, tetragonal		No	No	No		Yes		
Calcium	Ca_3P_2		2 51	Reddish brown crystals		Fast	Fast					
Carbon	C_3P			Yellowish white amorphous ppt.		No	No	No	No			
Chromium	CrP		5 3	Grey-black, orthorhombic		No		Slow	No	Slow		Yes
	Cr_3P	1515	6 1	Grey-black, tetragonal		No		Slow	No	Slow		Yes
Cobalt	CoP_3		4.26	Grey	−52	No						
	CoP		6 24	Grey, orthorhombic	−30	No						
	Co_2P	1386	6.4	Grey, orthorhombic	−43	No	Slow	Slow	No	Yes		Yes

Copper	CuP_2		4 20	Grey-black	−20	No	Slow	No		Yes		
	Cu_3P_2		6 35	Grey-black		No						
	Cu_2P		6 4	Grey-metallic		No	No	No		Yes		
	Cu_3P	1023	7 15	Steel grey, hexagonal	−32	No	Slow	No		Yes		
Gold	Au_2P_3		8 12	Grey powder		No	No	No		Yes		Yes
Iron	Fe_2P_2		4 95	Grey, orthorhombic	−34	No	Slow	Slow	No	Yes	Yes	Yes
	FeP		6 07	Grey, orthorhombic	−25	No	Slow	Slow	No	Yes	Yes	Yes
	Fe_2P	1370	6 77	Steel grey, hexagonal	−35	No	Slow	Slow	No	Yes	Yes	Yes
	Fe_3P	1166	7.11	Steel grey, tetragonal	−35	No	Slow	Slow	No	Yes	Yes	Yes
Lithium	Li_3P_5	ca. 650		Reddish brown powder		Fast	Fast					
	Li_3P		1 43	Dark colored, hexagonal		Fast	Fast					
Magnesium	Mg_3P_2		2 06	Yellowish grey transparent cubic		Fast	Fast					
Manganese	MnP_3		4 26(?)	Black powder		No						
	MnP	1147	5 34	Grey, orthorhombic		No	Slow			Yes		
	Mn_2P	1327	6 32	Grey, hexagonal		No						
	Mn_3P	1105		Tetragonal								
Molybdenum	MoP_2		5 35									
	MoP		6 58	Grey crystals, hexagonal		No	Slow			Yes		
	Mo_3P		9 07	Steel grey, tetragonal		No	No	No	No			

(continued)

TABLE 4-3 (*continued*)

Other element	Phosphide	Melting point (°C)	Density (g/cm.)	Color and crystal system	Heat of formation from red P and the metal (kcal)	Reaction with						
						Cold H_2O	Hot H_2O	Dilute acids	Dilute bases	Strong oxidizing acids	Strong bases	Alkaline melts
Nickel	NiP_3		4 19	Steel grey, hexagonal	−33	No						
	NiP_2		4 62	Steel grey, orthorhombic	−30	No						
	Ni_6P_5	1185	5 85	Steel grey crystals	−136	No						
	$Ni_{12}P$	1112	7 2	Steel grey, hexagonal	−40	No	No	No	No	Yes		
	Ni_5P_2	1185	7 5	Steel grey	−96	No	No	No	No	Yes		
	Ni_3P	975	7 7	Silvery grey, tetragonal	−48	No	No	No	No	Yes		
Platinum	PtP_2	ca. 1500	9 25	Steel grey, cubic		No	No	No	No	Slow		Yes
Potassium	K_2P_5	ca 650	ca. 2	Reddish brown		Fast	Fast					
Rhenium	ReP_3		7 30	Grey		No	No	No	No			
	ReP_2		8 83	Steel grey, cubic		No	No	No	No			
	ReP		12 0	Steel grey, cubic		No	No	No	No			
Rhodium	RhP_3		5 16	Steel grey		No	No	No	No	Slow		Yes
	Rh_2P Rh_3P	ca 1500	9 13	Steel grey, cubic		No	No	No	No	Slow		Yes
Silicon	SiP		ca 2 4	Light yellow powder		Slow	Yes					
Sodium	Na_2P_5	ca. 650		Reddish brown powder		Fast	Fast					
	Na_3P		1 74	Dark colored, hexagonal		Fast	Fast					

Strontium	Sr_3P_2		2	68	Brown crystals		Fast	Fast				
Tantalum	TaP_2		8	41	Black powder		No					
	TaP		10	9	Black powder, hexagonal		No					
Thorium	Th_3P_4		8	44	Greyish black, cubic		No	No	Slow			
	ThP		8	81	Greyish black, cubic		No	No				
Tin	SnP_3	580			Silvery white		No	Slow	No			
	Sn_3P_4	562			Silvery white		No	Slow	Slow	No	Yes	
	Sn_4P_3	550			Silvery white		No	Slow	Yes	No	Yes	
Titanium	TiP		3	95	Steel grey		No	No	No	No	Slow	No Yes
	$TiP_{0.95}$				Hexagonal		No					
Tungsten	WP_2		9	17	Black crystals		No	No	No	No	Slow	Yes
	WP		12	3	Steel grey, orthorhombic		No	No	No	No	Slow	Yes
Uranium	UP_2		8	57			No	No				
	U_3P_4		10	0	Greyish black, cubic		No	No	Yes			
	UP		10	2	Greyish black, cubic		No	No				
Vanadium	VP		4	7	Grey, hexagonal		No					
Zinc	ZnP_2	ca 700	3	0	Orange-red, pseudocubic		No	No	Slow		Yes	
	Zn_3P_2		4	7	Steel grey, tetragonal	−98	No	No	Slow		Yes	
Zirconium	ZrP_2		5.5		Grey		No	No	No	No	Slow	No Yes
	ZrP				Silvery grey, hexagonal		No	No	No	No	Slow	No Yes
	$ZrP_{0.90}$				Silvery grey, cubic							

in this field; but a number of the formulas which have been given for specific compounds are incorrect. In fact, in reviewing the literature on phosphides, Mellor[78] says "The subject generally wants overhauling, since many of the alleged phosphides hold a precarious position in the list of chemical individuals." Since the publication of Mellor's treatise, a considerable amount of x-ray, phase-diagram, and vapor-pressure work has been carried out which has resulted in a clear definition of the chemical individuality of a number of phosphides. Most of the discussion of phosphides given in this book is based on relatively recent papers; and the reader is referred to Mellor and Gmelin[78] for a more thorough review of the earlier literature.

Nearly all of the elements react with phosphorus, phosphorus vapor, or phosphine at elevated temperatures to form phosphides, the exact formula of which depends on the specific experimental conditions. Generally speaking, there are several different phosphides of each metallic element; although some metals have only one phosphide, and antimony, bismuth, lead, and mercury may not form any phosphides stable under normal conditions. Unlike alloys, the various crystalline species of the metal phosphides exhibit either a specific value of the metal-to-phosphorus ratio or a narrow range of values. In this respect, the phosphides are similar to salts. Some metal phosphides—such as Na_3P, Ca_3P_2, AlP, and Th_3P_4—have formulas which correspond to the classical valency rules; but this is far from common. Thus, the stable alkali metal phosphides exhibit an empirical formula M_2P_5.

The higher phosphides of a given metal usually decompose when heated to give a lower phosphide and phosphorus vapor. The phosphides of the alkali and alkaline earth metals react rapidly with cold water to form hydrogen phosphides (predominantly phosphine), whereas the phosphides of the elements of Groups IIIA, IVA, and VA do not. However, as a rule, these phosphides give hydrogen phosphides by reacting with dilute acids. The phosphides of the transition metals are considerably less reactive, and hot, strong, oxidizing acids or molten alkalies are usually needed to decompose them. Some of the transition-metal phosphides are extremely unreactive and only decompose when heated in strongly oxidizing atmospheres, such as Cl_2 or F_2. Thus, these particular phosphides can be considered as being among the more inert of all substances.

The properties of the binary phosphides are reported in Table 4-3,

[78] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longman's Green & Co., London, 1928, Vol. VIII, pp. 833–66. Also see the various volumes of L. Gmelin, *Gmelin's Handbuch der anorganischen Chemie*, Verlag-Chemie, Weinheim, Germany.

where the phosphides are arranged in the order of an alphabetical listing of the element combined with the phosphorus. Heats of formation of the phosphide from red phosphorus plus the other element in its thermodynamic standard state are shown in this table when available.

Preparation of Metal Phosphides

The simplest and most generally used method for preparing phosphides is to heat the metal with red phosphorus or phosphorus vapor in a nonoxidizing atmosphere. Hydrogen or carbon dioxide has often been used as a carrier for the phosphorus vapor, and large-scale preparation of some of the phosphides is often achieved by submerging white phosphorus in a bath of the molten metal so that phosphorus vapor is formed, only to be absorbed by the metal melt. In laboratory preparations, the volatile and easily oxidized metals are sometimes covered by a liquid such as paraffin oil while they are being reacted with phosphorus. Lithium chloride and tin phosphide have also been used as protective layers. Naturally, when an element forms several stable phosphides, the proper stoichiometric quantities must be used in the preparation.

In order to bring about the formation of thermally unstable phosphides (generally higher phosphides of a given metal), Biltz and coworkers[79] have used a modification of the procedure whereby phosphorus and the metal are reacted together. According to this technique, the synthesis is carried out at elevated temperatures, up to 1100°C., in an enclosed system using an excess of phosphorus. After heating for the desired length of time, the excess phosphorus is condensed in a slightly cooler portion of the apparatus. Since this reaction technique was first introduced to chemistry by Faraday, the term "Faraday method" may be applied to the procedure, which has been described in considerable detail in the literature.[80] When the reaction is allowed to take place above the boiling point of red phosphorus, considerable pressure may develop depending on the amount of excess phosphorus used, and the procedure is then referred to as the pressure (Druck) technique.

When a metal forms several phosphides, advantage may be taken of the fact that higher phosphides are often thermally unstable. For example, VP_2 has a vapor pressure of 760 mm. at 710°C., whereas VP has a negligible vapor pressure even at 1050°C.[81] Vanadium monophosphide can thus be

[79] W. Biltz and R. Juza, *Z. anorg. u. allgem. Chem.*, **190**, 161 (1930).

[80] H. Haraldsen, *Skrifter Norske Videnskaps-Akad., Oslo, Mat. Naturv. Kl.*, **1932**, No. 9, 1.

[81] M. Zumbusch and W. Blitz, *Z. anorg. u. allgem. Chem.*, **249**, 30 (1941).

prepared by heating the diphosphide in a vacuum at elevated temperatures. Of course it should be noted that, when the lower phosphides are also unstable, this method may produce a mixture of phosphides and/or the metal. Thermally stable phosphides are sometimes conveniently prepared by heating a higher phosphide with a stoichiometric amount of the metal. Thus, V_3P can be made by heating vanadium with vanadium monophosphide which, in turn, was prepared by decomposing the diphosphide.[81]

Instead of using red phosphorus or phosphorus vapor, phosphine may be passed over the hot metal to make the lower phosphides. In several cases, phosphides have been prepared by reacting the metal chloride with phosphine to give the metal phosphide plus hydrogen chloride vapor. Examples[82] are the formation of WP_2, ZrP_2, and TiP. Reaction of phosphine with solutions of metal salts often gives phosphides which may contain unsubstituted hydrogen. With metal salts the phosphides of which are not very stable, a mixture of phosphides and the metal is often formed. As would be expected, when phosphine reduces the metal salt to the metal, it is simultaneously oxidized to the oxyacids of phosphorus. By using an excess of phosphine, a number of allegedly pure metal phosphides have been made. Preparation of Ag_3P, Cu_3P, Au_3P, Hg_3P, Hg_3P_2, Pb_3P_2, Cd_3P_2, and Cu_3P_2 by this procedure has been reported.[83] White phosphorus reacts in a manner similar to phosphine with solutions of metal salts. However, this reaction is usually not used as a preparative procedure, since the resulting phosphide forms a coating over the phosphorus, when present either in liquid or solid form, which greatly slows down the reaction and can lead to an impure product. A few experiments have been carried out on the reactions between phosphine or phosphorus and the alkali metals in liquid ammonia. However, the initial products are often not normal phosphides but are hydrogen-containing compounds analogous to the amides and imides.

Phosphides can also be made by reducing salts of the oxyacids with carbon, hydrogen, and other reducing agents. Usually phosphates are reduced in this manner at red heat. High-temperature electrolysis of fused sodium phosphates containing oxides or salts of heavy metals has been used to obtain the phosphides of several metals. By controlling the composition of the melt, the temperature, and the current density, different phosphides of a given metal can be produced. Some phosphides, such as W_4P,

[82] E. D. Defacqz, *Compt. rend.*, **130**, 915 (1900); *ibid.*, **132**, 32 (1901); J. Gewecke, *Liebig's Ann.*, **361**, 79 (1908).

[83] L. Moser and A. Brukl, *Z. anorg. u allgem. Chem*, **121**, 73 (1922); A. Brukl, *ibid*, **125**, 252 (1922).

which cannot be obtained by any other method are made in this manner.[84] This technique has been discussed in two reviews.[85]

Alkali Metal Phosphides

The best-known and well-established phosphides[86,87] of the alkali metals have the formula M_2P_5, where M stands for Li, Na, K, Rb, or Cs. These phosphides are thermally stable up to temperatures near 650°C. and, as they are usually prepared,[87] exhibit a reddish brown color. They react instantly with water or with moisture in the air to form phosphine.

In addition to the compounds with the formula M_2P_5, lithium and sodium also form compounds having the approximate composition M_3P.[88] When the stoichiometric amounts of sodium or lithium are heated with phosphorus under a layer of lithium chloride, a product having less alkali metal than corresponds to the M_3P composition is obtained. X-ray examination[88] of these materials showed the presence of a phase which is similar in structure to the known compound Na_3As. No chemical analyses have been made on reliable preparations of Li_3P or Na_3P, and their existence is based wholly on this x-ray evidence. By this same criterion, K_3P, Rb_3P, and Cs_3P do not seem to exist.

As shown in Table 4-4, both Na_3P and Li_3P have crystal structures[88] of the trisodium arsenide (Na_3As) type, so that the comments given below for Na_3P are true for Li_3P, except that the interatomic distances will be different. According to the detailed structure of these crystals, there are two locations for the alkali metal atoms. In one location, each sodium has three neighboring phosphorus atoms surrounding it in the same plane at a distance of 2.88 A. between atom centers. In addition, there are six nearest-neighbor sodium atoms at a distance of 3.24 A. The six sodium atoms are arranged so as to form a trigonal prism with the three neighboring phosphorus atoms being outside the square faces of this prism. The arrangement of nearest-neighbor atoms around this sodium is shown on the next page.

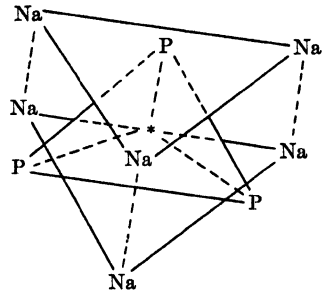
[84] M. C. Neuberger, *Z. Krist.* **93**, 1 (1936), also see ref. 164.

[85] J. L. Andrieux, *Rev. mét.*, **45**, 49 (1948); *J. four élec.*, **57**, No. 3, 54 (1948); M. Chêne, *Ann. Chim.*, **15**, 187 (1941).

[86] E. Zintl and G. Woltersdorf, *Z Elektrochem.*, **41**, 876 (1935); V. A. Pleskov and M. Monoszon, *Acta Physicochem. U.S.S.R.*, **1**, 725 (1935).

[87] L. Hackspill and R. Bossuet, *Compt. rend.*, **154**, 209 (1912); *ibid.*, **157**, 720 (1913)

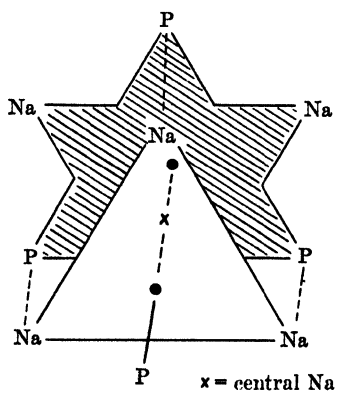
[88] G. Brauer and E. Zintl, *Z. physik. Chem.*, **B37**, 323 (1937).



(4-28)

* = central Na atom

In the other location, there are two sodium atoms for each atom in the first sodium location. Each of the sodium atoms in this second location has one phosphorus atom directly below it, at a distance of 2.93 A. There are also three phosphorus atoms forming an equilateral triangle in a plane situated above the sodium atom in question. The Na-P distance in this case is 3.24 A. These four nearest-neighbor phosphorus atoms thus form a distorted tetrahedron about the sodium atom. In addition, the sodium atoms in this location have six nearest-neighbor sodium atoms at a distance of 3.24 A., with a seventh neighboring sodium atom directly above it at 2.93 A. Three of these atoms are in the same plane as the triangle of nearest-neighbor phosphorus atoms but form an equilateral triangle which is rotated 60° from the phosphorus triangle. The other three sodium atoms are also in the form of a triangle, but this triangle lies directly under that formed by the phosphorus and is also below the central sodium atom. The arrangement of nearest neighbors about this sodium is shown below; where the seventh neighboring sodium atom directly above the central one is hidden by the star formed by alternate sodium and phosphorus atoms:

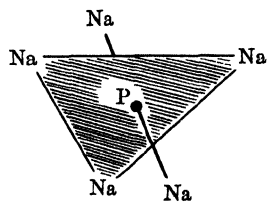


(4-29)

x = central Na atom

In the first position, each sodium atom is surrounded by six other sodium atoms in an arrangement similar to hexagonal close packing of spheres, whereas in the second position the six nearest sodium atoms surround the given sodium atom as in cubic close packing of spheres. In both cases, the sodium atoms are placed with respect to their nearest sodium neighbors in an arrangement which is common to metals. It should be noted that in this structure the Na-Na distances are 12% smaller than in metallic sodium (in which the Na-Na coordination number is 8 instead of 6). For Li_3P, the Li-Li distance is 8% smaller than in the metal.

Each phosphorus atom in Na_3P is surrounded by five nearest-neighbor sodium atoms, with six additional sodium neighbors at a further distance (3.42 A.). Three of the nearest-neighbor sodiums form an equilateral triangle in the center of which lies the phosphorus. The Na-P distance in this case is 2.88 A. Directly above and directly below this central phosphorus are sodium atoms. The Na-P distance for these two sodiums is 2.93 A. Thus, the phosphorus atom in Na_3P has its five nearest-neighbor sodium atoms arranged at the corners of a trigonal bipyramid having the same general geometry as the five halide atoms in the phosphorus pentahalides. This arrangement is shown below:



(4-30)

If the phosphorus covalent radius of 1.1 A. is subtracted from the Na-P distance, a sodium radius of 1.8 A. is obtained. Likewise, if the Na-Na distance observed in Na_3P is divided in half, a sodium radius of 1.6 A. results. The accepted radius for the sodium atom in metals is 1.8 A., whereas its accepted radius in ionic compounds is 1.0 A. Moreover, an extrapolation of covalent radii—such as is given in Figure 2-3—leads to a covalent radius of 1.4 A. for sodium. One can conclude from this that in the Na_3P crystal, the sodium atoms exhibit bonding that is somewhat similar to that found in metals. On the other hand, Na_3P can probably not be considered as an interstitial compound similar to the borides, carbides, nitrides, and phosphides of the transition metals. In these interstitial compounds, the metal-to-metal distance is larger in the phosphide than in the metal, whereas in Li_3P and Na_3P the reverse is true. In other words, the alkali-metal atoms in Li_3P and Na_3P have effectively "shrunk" when the phosphorus atoms

were introduced. This implies that the metallic bond exhibits appreciable covalent or ionic character in these compounds.

The phosphorus in this compound is surrounded by sodium atoms situated at the corners of a trigonal bipyramid. This means that, if the phosphorus is covalently bonded to its neighboring sodium atoms, the base σ-bond structure corresponds to sp^3d-hybridization. In the phosphorus pentahalides where there is little question about the sp^3d-base structure, the two apical halide atoms are at a slightly greater distance than the other three halides, so that the geometry is the same as in the Na_3P and Li_3P crystals Although the evidence is far from conclusive, it appears that the phosphorus in Li_3P and Na_3P may be covalently bound to its neighboring atoms and exhibits the symmetry ascribed to sp^3d-hybridization Because it is thought that the bonds from the phosphorus are primarily covalent with some ionic character, the bonds between sodium atoms are probably part way between metallic and covalent bonds.

The structure of Na_3P was discussed in considerable detail because, if there is any chance that a phosphide ion exists, it probably should be found in binary compounds with the alkali metals. Detailed structure analysis of the two alkali metal phosphides for which x-ray data are available gives no particular support to the concept of phosphide ions. On the other hand, these measurements do not definitely demonstrate that phosphide ions are nonexistent in these crystals. However, the most reasonable interpretation of the data does not support the idea of phosphide ions, and we can probably assume that the phosphorus is connected to its neighboring atoms by bonds which are primarily covalent in character.

Phosphine or phosphorus reacts with the alkali metals in liquid ammonia to give hydrogen gas and solid reaction products which, upon evaporation of the ammonia, are usually found to contain nitrogen. In a recent study[89] it was shown that when lithium, sodium, or potassium in liquid ammonia was titrated with a solution of phosphorus in toluene, there were definite changes in color which were attributed to compound formation. At the start of the titration, the ammonia exhibited a deep blue color due to the alkali metal. As the reaction proceeded, the blue color showing up in the ammonia first changed to a greenish cast, then to a deep yellow-green color, and finally there was a distinct end-point color change to yellow tinged with orange. This definite color change corresponded to Li/P and Na/P mole ratios of 2 and a K/P mole ratio of 1.5. Interpretation of the chemical properties of these solutions indicated that the sodium and lithium phosphides thus formed are derivatives of diphosphine corresponding to the formula,

M_2PPM_2[89] However, a solid compound taken from solution and formulated as $Na_2PPNa_2 \cdot 2NH_3$ by Evers and coworkers was later stated by others[90] to be a mixed phosphide-amide having the formula $NaHPPH\text{-}Na \cdot 2NaNH_2$. In reality, there is not much evidence to show that either formula is right; and, in all caution, the compound should probably be written in terms of its empirical composition, *viz.*, Na_2PNH_x where x is probably 3.

When phosphine was passed into a solution of lithium in liquid ammonia at −80°C., the blue solution became yellow-colored in the same way as was found when elemental phosphorus was added to the alkali metal in liquid ammonia.[91] Upon evaporation of the liquid ammonia, a white microcrystalline powder was formed. Measurement of the phosphine absorbed and hydrogen evolved during the reaction showed that 1 mole of PH_3 was taken up per mole of Li to give $^1/_2$ mole of H_2. Reaction of the white microcrystalline powder with water showed that there were 4 moles of NH_3 per mole of Li. This leads to the empirical formula $LiPH_2 \cdot 4NH_3$ for the white powder[91] which reacts vigorously with water to give PH_3 plus a mixture of LiOH and NH_4OH. Upon heating,[92] the compound $LiPH_2 \cdot 4NH_3$ loses first 2 and then 1 mole of NH_3. Removal of the last mole of NH_3 results in the simultaneous loss of approximately $^1/_2$ mole of PH_3 per formula weight of the phosphide. This decomposition takes place at 50°C., leaving a residue having the empirical composition Li_2PH.

When monosodium phosphine, exhibiting the empirical formula $NaPH_2$ is made in liquid ammonia, it is difficult if not impossible to obtain a nitrogen-free solid product. However, this has been accomplished by working in organic solvents.[93] Thus, the purest form of $NaPH_2$ has been made by blowing a vigorous current of phosphine into ether to which was added gradually a solution of triphenylmethyl sodium, $(C_6H_5)_3CNa$, in ether—so that phosphine is always present in excess. The $NaPH_2$ is produced as a pure white flocculent precipitate which ignites spontaneously in air but can be stored indefinitely in an inert atmosphere. In water this compound decomposes instantly into phosphine and sodium hydroxide. When the sodium or potassium compounds $NaPH_2$ or KPH_2 are heated,[92] there is first an evolution of phosphine (at 70°C. for the sodium derivative and at

[89] E. C. Evers, *J. Am. Chem. Soc.*, **73**, 2038 (1951); E. C. Evers, E. H. Street, and Shee Lup Jung, *ibid.*, **73**, 5088 (1951); E. C. Evers and J. M. Finn, *J. Phys. Chem.*, **57**, 559 (1953).

[90] P. Royen and W. Zschaage, *Z. Naturforsch.*, **86**, 777 (1953).

[91] C. Legoux, *Compt. rend.*, **207**, 634 (1938).

[92] C. Legoux, *Bull. soc. chim.*, **7**, 545 (1940).

[93] H. Albers and W. Schuler, *Ber.*, **76B**, 23 (1943).

TABLE 4-4
Structure of Some Phosphides for Which Adequate X-Ray Data Are Available

Compound	Crystal system	Space group	Formula weights per unit cell	Cell dimensions	Number of atoms surrounding a specified atom at the distances given		Data for the metal in elemental form	Structure prototype[a] and isomorphs	Refs.[b]
Li_3P	Hexagonal	C6/mmc	2	a = 4.264 c = 7.579	P: 3 Li_I 2.46 A.; 2 Li_{II} 2.53; 6 Li_{II} 2.77; 6 P 4.26; 6 P 4.52	Li_I: 3 P 2.46 A.; 6 Li_{II} 2.77; 2 Li_I 3.79 2 Li_{II}: 1 P 2.53 A.; 3 P 2.77; 3 Li_I 2.77; 3 Li_{II} 2.77	8 Li at 3.033 A	**Na_3As** Li_3As α-Li_3Sb Na_3Bi Na_3Sb K_3Bi K_3Sb K_3As	88 [V, 6-7] [V, 59-60]
Na_3P	Hexagonal	C6/mmc	11	a = 4.980 c = 8.797	P: 3 Na_I 2.88 A.; 2 Na_{II} 2.93; 6 Na_I 3.24; 6 P 4.98	Na_I: 3 P 2.88 A; 6 Na_{II} 3.24; 2 Na_I 4.40 (2) Na_{II}: 1 P 2.93 A.; 3 P 3.24; 3 Na_I 3.24; 3 Na_{II} 3.24	8 Na at 3.708 A.	As above	As above
LiZnP	Cubic		4	a = 5.78	P: 4 Li 2.50 A.; 4 Zn 2.50; 12 P 4.25	Li: 4 P 2.50 A.; 6 Zn 2.89; 6 Li 2.89 Zn: 4 P 2.50 A.; 6 Li 2.89; 6 Zn 2.89	See Li_3P and Zn_3P_2	**Anti-CaF_2**	94 [XIII, 30]

LiMgP	Cubic	Fm3m	4	a = 6 02	P: (0 or 4) Li_T — 2 61 A; (12 or 0) Li_O — 3 01; 4 Mg — 2 61; 12 P — 4 25	Li_T: 4 P — 2 61 A.; (0 or 4) Li_O — 2 61; (6 or 0) Li_T — 3 01; 6 Mg — 3 01	See Li_3P and Mg_3P_2	Anti-CaF_2 with interstitial atoms	
						Li_O: (0 or 4) Li_T — 2 61 A.; (12 or 0) Li_O — 4 25; 4 Mg — 2 61; 6 P — 3 01			94 [XIII, 30]
Mg_3P_2	Cubic	Ia3	16	a = 12 01	P_I: 6 Mg — 2 6 A; 6 P_{II} — 4 0; 6 P_{II} — 4 4	(6) Mg: 1 P_I — 2 6 A.; 1 P_{II} — 2 2; 1 P_{II} — 2 9; 1 P_{II} — 3 0; 3 Mg — 3 2; 3 Mg — 4 1	6 Mg at 3.191 A. also 6 Mg at 3 203 A.	Anti-Mn_2O_3 Also an anti-structure to Sc_2O_3, Y_2O_3, In_2O_3	95, 97 [III, 353–7 [Also see II, 40–1]
					(3) P_{II}: 2 Mg — 2 2 A; 2 Mg — 2 9; 2 Mg — 3 0; 2 P_I — 4 0; 2 P_I — 4 4; 4 P_{II} — 4 0; 4 P_{II} — 4 5				
AlP	Cubic	$F\bar{4}3m$	4	a = 5.42	P: 4 Al — 2 35 A; 12 P — 3 84; 12 Al — 4 50	Al: 4 P — 2 35 A.; 12 Al — 3 84; 12 P — 4 50	12 Al at 2 858 A.	ZnS CuCl CuBr CuI BeS CdS HgS BeSe ZnSe CdSe HgSe BeTe	102, 103 [I, 76–7, 140, 772] [II, 236]

(*continued*)

TABLE 4-4 (*continued*)

Compound	Crystal system	Space group	Formula weights per unit cell	Cell dimensions	Number of atoms surrounding a specified atom at the distances given	Data for the metal in elemental form	Structure prototype[a] and isomorphs	Refs.[b]
GaP	Cubic	$F\bar{4}3m$	4	a = 5.436 A.	P: 4 Ga 2.36 A.; 12 P 3.85; 12 Ga 4.51 Ga: 4 P 2.36 A; 12 Ga 3.85; 12 P 4.51	At 2.44 and at 2.71 A	As above	102, 103 [I, 76–7,140, 772] [II, 236]
Cu_3P	Hexagonal	$C\bar{3}c$	6	a = 7.070 A c = 7.135	(3) P: 2 Cu_{II} 2.28 A; 2 Cu_{III} 2.33; 2 Cu_{III} 2.41; 2 Cu_{III} 2.50; 2 Cu_I 3.23; 2 Cu_{II} 3.73; 2 P 3.96; 4 P 4.47 Cu_I: 6 Cu_{III} 2.54 A; 2 Cu_I 3.57; 6 Cu_{II} 4.26; 3 P 3.23 (2) Cu_{II}: 6 Cu_{III} 2.64 A.; 2 Cu_{II} 3.57; 3 Cu_I 4.26; 3 P 2.28; 3 P 3.73 (6) Cu_{III}: 1 Cu_I 2.54 A; 1 Cu_{III} 2.57; 1 Cu_{III} 2.62; 2 Cu_{II} 2.64; 2 Cu_{III} 2.73; 1 Cu_{II} 2.78; 1 P 2.33; 1 P 2.41; 1 P 2.50	12 Cu at 2.55 A.		129 [VI, 7–9, 65–7] [VII, 99] [XI, 119]

Zn_3P_2	Tetragonal	$P4_2/nmc$	8	a = 8.09 A c = 11.45	P_I: 2 Zn_{III} 2.35 A.; 2 Zn_I 2.44; 4 Zn_{II} 2.77; 4 P_{III} 3.96; 4 P_{II} 4.05; 4 P_{III} 4.13	Zn_{II}: 2 P_{III} 2.35 A; 1 P_{II} 2.44; 1 P_I 2.77; 1 Zn_{III} 3.00; 2 Zn_{III} 3.07	6 Zn at 2.660 A. Also 6 Zn at 2.907 A.	Cd_3P_2 Zn_3As_2 Cd_3As_2	139 [III, 51-3, 353-7]
Cd_3P_2	Tetragonal	$P4_2/nmc$	8	a = 8.74 A c = 12.28	P_I: 2 Cd_{III} 2.55 A; 2 Cd_I 2.62; 2 Cd_{II} 2.99; 4 P_{III} 4.26; 4 P_{II} 4.34; 4 P_{III} 4.45	Cd_{II}: 2 P_{III} 2.55 A; 1 P_{II} 2.62; 1 P_I 2.99; 1 Cd_{III} 3.22; 2 Cd_{III} 3.33	6 Cd at 2.973 A Also 6 Cd at 3.287 A	Zn_3P_2 Zn_3As_2 Cd_3As_2	139 [III, 51-3, 353-7]
Th_3P_4	Cubic	$I\bar{4}3d$	4	a = 8.600 A	(4) P: 6 Th 2.98 A.; 3 P 3.20; 2 P 3.72; 6 P 4.24; 6 P 5.36	(3) Th: 8 P 2.98 A.; 8 Th 4.02; 4 Th 5.31; 8 Th 5.88	12 Th at 3.590 A		144 148
TiP	Hexagonal	$P6_3/mmc$	4	a = 3.487 A c = 11.65	P: 6 Ti 2.48 A; 6 P 3.49; 6 P 3.54	Ti: 6 P 2.48 A; 1 Ti 2.91	6 Ti at 2.91 A Also 6 Ti at 2.95 A	**MoC** β-ZrP NbN	149
α-ZrP	Cubic	Fm3m	4	a = 5.27 A	P: 6 Zr 2.64 A.; 12 P 3.73	Zr: 6 P 2.64 A; 12 Zr 3.73	6 Zr at 3.17 A and 6 Zr at 3.22 A.	**NaCl**	149
β-ZrP	Hexagonal	$P6_3/mmc$	4	a = 3.677 A c = 12.52	P: 6 Zr 2.64 A.; 6 P 3.68; 6 P 3.78	Zr: 6 P 2.64 A; 1 Zr 3.13	As above	**MoC** TiP NbN	149
VP	Hexagonal	$P6_3/mmc$	2	a = 3.18 A c = 6.22	P: 6 V 2.41 A; 6 P 3.18; 6 P 3.61	V: 6 P 2.41 A; 2 V 3.11	8 V at 2.627 A	**NiAs**	149

(continued)

TABLE 4-4 (*continued*)

Compound	Crystal system	Space group	Formula weights per unit cell	Cell dimensions	Number of atoms surrounding a specified atom at the distances given		Data for the metal in elemental form	Structure prototype[a] and isomorphs	Refs.[b]
α-NbP	Hexagonal	F4/mmm	4	a = 3.32 A. c = 5.69	P: 4 Nb 2.35 A.; 4 P 3.32; 4 Nb 3.29; 4 P 3.29	Nb: 4 P 2.35 A.; 4 Nb 3.29; 4 P 3.29	8 Nb at 2.853 A.	α-TaP	149
β-NbP	Hexagonal	$I4_12$	4	a = 3.325 A. c = 11.38	P: 4 Nb 2.35 A.; 4 P 3.32; 4 P 3.30	Nb: 4 P 2.35 A.; 4 Nb 3.32	As above	β-TaP	149
α-TaP	Hexagonal	F4/mmm	4	a = 3.320 A. c = 5.69	P: 4 Ta 2.35 A.; 4 P 3.32; 4 Ta 3.30; 4 P 3.30	Ta: 4 P 2.35 A.; 4 Ta 3.30; 4 P 3.30	8 Ta at 2.854 A.	α-NbP	149
β-TaP	Hexagonal	$I4_12$	4	a = 3.330 A. c = 11.39	P: 4 Ta 2.36 A.; 4 P 3.33; 4 P 3.30	Ta: 4 P 2.36 A.; 4 Ta 3.33	As above		149
CrP	Orthorhombic	Pb/nm	4	a = 6.108 A. b = 5.36 c = 3.113	P: 2 Cr 2.25 A.; 2 Cr 2.27; 1 Cr 2.37; 2 P 3.08; 2 P 3.11	Cr: 2 P 2.25 A.; 2 Cr 2.48; 2 P 2.27; 1 P 2.37	8 Cr at 2.492 A.	MnP	149
MoP	Hexagonal	$P\bar{6}m2$	1	a = 3.23 A c = 3.20	P: 6 Mo 2.46 A.; 2 P 3.20; 6 P 3.23	Mo: 6 P 2.46 A; 2 Mo 3.20	8 Mo at 2.720 A.	WC	149
WP	Orthorhombic	Pbnm	4	a = 6.219 A. b = 5.717 c = 3.238	P: 2 W 2.38 A.; 2 W 2.43; 1 W 2.55; 2 P 3.18; 2 P 3.24	W: 2 P 2.38 A.; 2 P 2.43; 1 P 2.55; 2 W 2.71	8 W at 2.735 A. In β-form at 2.519 and at 2.816.	MnP	149

MnP	Orthorhombic	Pbnm	4	$a = 5.905$ A. $b = 5.249$ $c = 3.167$	P: 1 Mn 2 30 A.; 2 Mn 2 32; 2 Mn 2 38; 1 Mn 2 39; 2 P 2 68	Mn: 1 P 2 30 A.; 2 P 2 32; 2 P 2 38; 1 P 2 39; 1 Mn 2 69; 1 Mn 2 74; 4 Mn 2 84	At 2.24 A. and at 2 38 A.	WP	A [III, 17–8, 263–4]
Fe_2P	Hexagonal	$C\bar{6}m2$	3	$a = 5.85$ A. $c = 3.45$	P_I: 6 Fe_I 2 30 A.; 3 Fe_{II} 2 34; 2 P_I 3 45; 6 P_{II} 3 67 (2) P_{II}: 3 Fe_{II} 2 19 A; 3 Fe_I 2 24; 2 P_{II} 3 45; 3 P_{II} 3 49; 3 P_I 3 67	(3) Fe_I: 2 P_{II} 2 24 A.; 2 P_I 2 30; 2 Fe_I 2 63; 6 Fe_{II} 2 63 (3) Fe_{II}: 2 P_{II} 2 19 A.; 1 P_I 2 34; 6 Fe_I 2 63; 2 Fe_{II} 3 10; 2 Fe_{II} 3 45	In α-Fe at 2.478 A. and in γ-Fe at 2 52 A.	Ni_2P	B [II, 15–6, 284–5]
FeP_2	Orthorhombic	Pnnm	2	$a = 2.75$ A. $b = 4.98$ $c = 5.66$	(2) P: 1 P 2.17 A.; 1 Fe 2 24; 2 Fe 2.30; 2 P 2 73; 4 P 3 15; 4 P 3 27; 1 P 3 70	Fe: 2 P 2 24 A.; 4 P 2 30; 2 Fe 2 73; 8 Fe 4 01	As above	FeS_2 $FeAs_2$ $FeSb_2$	C [III, 310]
Rh_2P	Cubic	Fm3m	4	$a = 5.50$ A.	P: 8 Rh 2 38 A.; 12 P 3 89	(2) Rh: 4 P 2 38 A.; 6 Rh 2 75		Anti-CaF_2, Ir_2P	148
Ir_2P	Cubic	Fm3m	4	$a = 5.54$ A.	P: 8 Ir 2 40 A.; 12 P 3 91	(2) Ir: 4 P 2 40 A.; 6 Ir 2 77	12 Ir at 2.709 A.	Anti-CaF_2, Rh_2P	148

[a] The structure prototypes are in bold face type. Those bold face structures have arbitrarily been chosen by crystallographers as comparison standards.

[b] References to *Strukturbericht* and to its successor *Structure Reports* (issued by the Crystallographic Society) are given in brackets, [ ]. The Roman numeral refers to the volume number and the Arabic numbers to the pertinent pages. Other references denoted by capital letters are the following:

A. K. E. Fylking, *Arkiv Kemi Mineral. Geol.*, 11B, No. 48, 1 (1934).

B. S. B. Hendricks and P. R. Kosting, *Z. Krist.*, 74, 511 (1930); J. B. Friauf, *Trans. Am. Soc. Steel Treating*, 17, 499 (1930).

C. K. Meisel, *Z. anorg. u. allgem. Chem.*, 218, 360 (1934).

100°C. for the potassium derivative), followed by release of hydrogen (at 100°C. for $NaPH_2$ and 175°C. for KPH_2). At temperatures around 350°C., some of the alkali metal also distills out of the material to leave as a final product the thermally stable compounds Na_2P_5 and K_2P_5, respectively.

A series of mixed phosphides of lithium and other metals has been reported.[94] The formulas of these phosphides are LiMgP, LiZnP, Li_3AlP_2, Li_3GaP_2, Li_5SiP_3, Li_5GeP_3, and Li_5TiP_2. All of them exhibit a high electrical resistance (specific resistance of pressed pieces $> 10^6$ ohms) and melt at temperatures greater than 900°C. These mixed phosphides are all colored brown. An x-ray structure study has been interpreted[94] to mean that, in LiZnP, each kind of atom has a fixed position but, in the other compounds, the Li atoms are statistically distributed in the structure. The structural data for LiZnP and LiMgP are presented in Table 4-4.

Alkaline Earth Metal Phosphides

All of the alkaline earth metals form phosphides having formulas predicted by classical valence rules, *viz.* M_3P_2. These compounds can be prepared by reacting[78] the metal with red phosphorus in a sealed tube and subliming away the excess phosphorus or by passing phosphorus vapor[78,95] in a stream of hydrogen over the metal at 750°C. and again volatilizing the excess phosphorus. Calcium, strontium, and barium phosphides have also been made by heating the corresponding phosphate with carbon in an electric arc.[78] Calcium phosphide can also be prepared by heating calcium and red phosphorus together under a layer of petroleum.[78] In a recent report[96] it was claimed that barium and red phosphorus react at temperatures in the range of 400–450°C. to produce a crystalline material having the empirical formula BaP_3. On heating, this substance loses phosphorus in the temperature range of 740–780°C. to form a substance having the empirical formula BaP_2, which, in turn, loses phosphorus at a still higher temperature to form the well-known Ba_3P_2.

All of the alkaline earth sesquiphosphides, M_3P_2, are stable on heating in hydrogen at 750°C. In an inert gas, barium sesquiphosphide is found to be unaffected by heating at 840°C.; calcium sesquiphosphide can be heated as high as 1250°C. without decomposition. However, all of these

[94] R. Juza and W. Schulz, *Z. anorg. u. allgem. Chem.*, **275**, 65 (1954).

[95] E. Zintl and Z. Huseman, *Z. physik. Chem.*, **21B**, 138 (1933); M. von Stackelberg and R. Paulus, *ibid.*, **22B**, 305 (1933).

[96] S. A. Shchukarev, M. P. Morozoba, and E. A. Prokofyeva, *Zhur. Obshcheĭ Khim.*, **24**, 1217 (1954).

phosphides react rapidly with moist air to liberate phosphine. When treated with water, all of the alkali metal phosphides liberate phosphine. At temperatures around 300°C., the alkaline earth sesquiphosphides begin to react rapidly with oxygen, becoming incandescent. Beryllium and calcium sesquiphosphides are reported to exhibit a brown color, while the color of magnesium sesquiphosphide has been reported to range from yellow-green to orange. Barium sesquiphosphide has been described as a black crystalline mass. Magnesium sesquiphosphide is said to be transparent and to have a high electrical resistance (typical nonconductor).

The crystal structures of Be_3P_2, Mg_3P_2, and Ca_3P_2 have been investigated by x-ray,[95,97] and a complete structure analysis has been obtained for the beryllium and magnesium phosphides, as shown for the latter in Table 4-4. Beryllium and magnesium sesquiphosphides exhibit a cubic anti-manganese oxide structure in which there are two slightly different positions for the phosphorus atoms. In Mg_3P_2, each magnesium atom is surrounded by four phosphorus atoms so that it is in the center of a distorted tetrahedron. All four Mg-P distances are different (2.2, 2.6, 2.9, and 3.0 A.), with an average value of 2.7 A. Each magnesium atom is also quite close (3.2 A.) to three other magnesium atoms, which are so arranged that the Mg-Mg axes are 90° apart—in other words, if the given magnesium atom is situated at the corner of a 3.2 A. cube, the three nearest magnesium atoms are at adjacent corners. In magnesium metal, the Mg-Mg distance is 3.20 A. Thus, the Mg-Mg distance in the phosphide is the same as in the metal, but the coordination number of nearest neighbors is three in the phosphide instead of six as in the metal.

In either position, each phosphorus atom is surrounded by six magnesium atoms arranged at the corners of a tetragonal bipyramid. In one position, the Mg-P distances are all the same and equal 2.6 A.; in the other, the phosphorus atom is not centered in the tetragonal bipyramid, so that there are three different Mg-P distances (2.2, 2.9, and 3.0 A.), which average 2.7 A. The distances between phosphorus atoms are all equal to or greater than 4 A., so that the phosphorus atoms can be considered as being isolated from each other. The arrangement of the magnesium atoms around the phosphorus suggests the sp^3d^2 hybridization of the phosphorus. The structures of the alkaline-earth sesquiphosphides probably partake about equally of metallic and covalent character. If it is assumed that a phosphide ion (P^{3-}) is present, its radius would be about 2.0 A.; *i.e.*, 2.6–0.65 A., where 0.65 A. is the accepted ionic radius of Mg^{2+}.

The partial pressure of phosphorus over a mixture of Ca_3P_2 plus cal-

[97] M. V. Stackelberg, *Z. physik. Chem.*, **B27**, 53 (1934).

cium phosphates has been measured.[98] This pressure, given by the following equations, represents the partial pressure of P_4 gas over Ca_3P_2, where the solid residue (Ca?) undoubtedly reacts with the calcium phosphates present to form unspecified reduction products:

$$\log p_{\text{mm.}} = -6080/T + 6.104 \qquad \text{for } 1473° < T < 1595°\text{K.} \quad (4\text{-}31)$$

and

$$\log p_{\text{mm.}} = -7760/T + 7.160 \qquad \text{for } 1595° < T < 1773°\text{K.} \quad (4\text{-}32)$$

As is the case with the alkali metals, phosphides (often poorly defined) of the alkaline earth metals can be made by adding phosphorus or phosphine to liquid ammonia containing the metal.[99] Thus, a compound having the empirical formula $Ca(PH_2)_2 \cdot 6NH_3$ is made by reacting phosphine with calcium in liquid ammonia. This substance loses 4 moles of ammonia when put in a vacuum at 0°C. Upon heating in the vacuum, a material with the empirical formula CaHP is formed which, at higher temperatures, decomposes further.

Phosphides of Group IIIA Elements

Boron phosphide, BP, has recently been prepared[100] through the reaction between boron and phosphorus in evacuated silica tubes. It has a cubic structure of the zinc-blend type, with a cube edge of 4.538 A. The B-P distance is 1.964 A., and both elements exhibit four-fold coordination. This means that both atoms have an octet of electrons and exhibit an sp^3 type of hybridization. According to the early work[100] on boron phosphides, BP can be made by heating the addition product $BBr_3 \cdot PH_3$ to 300°C. It can also be prepared by heating one of the boron phosphoiodides, BPI_2 or BPI to about 500°C. in a stream of hydrogen. Boron phosphide is a maroon or black powder insoluble in all solvents which were tested. Boiling water has no action on the phosphide, but it is decomposed by boiling concentrated alkalies with the evolution of phosphine and by steam at 400°C. with the formation of boric acid and phosphine. Dilute or concentrated hydrochloric or sulfuric acids have no action on boron phosphide in the cold. When boron monophosphide is heated to about 1000°C. in a stream of hydrogen,

[98] H. H. Franck and H. Füldner, *Z. anorg. u. allgem. Chem.*, **204**, 97 (1932).

[99] C. Legoux, *Compt. rend.*, **209**, 47 (1939); *Ann. chim.*, **17**, 100 (1942).

[100] S. Rundqvist, paper at the XVIth International Congress of Pure and Applied Chemistry, Paris, 1957; P. Popper and T. A. Ingles, *Nature*, **179**, 1075 (1957); H. Moissan, *Ann. chim. Phys.*, **6**, No. 7, 296 (1895); *Ccmpt. rend.*, **113**, 787 (1891); A. Besson, *ibid.*, **110**, 80, 516 (1890); *ibid.*, **113**, 78 (1891).

it forms the compound B_6P_5. This compound is even more inert than BP, since it does not burn in an atmosphere of chlorine below a dull red heat and is not attacked by nitric acid. It can be decomposed, however, by molten alkali metal nitrates.

According to Moissan,[100] boron phosphodiiodide, BPI_2, can be prepared by reacting a solution of boron triiodide in carbon disulfide with a similar solution of phosphorus in the absence of moisture. The product BPI_2 is a finely divided dark red powder which melts at about 195°C. and volatilizes in a vacuum at about the same temperature. After sublimation, BPI_2 is obtained as a well-crystallized red product. The compound is very slightly soluble in carbon disulfide and is insoluble in benzene, phosphorus trichloride, and carbon tetrachloride. It is very hygroscopic and decomposes rapidly in moist air. It also decomposes in water giving hydriodic, phosphorous, and boric acids plus some phosphine in the presence of a large amount of water, and these products plus a detectable amount of phosphonium iodide and a yellow precipitate which might be the solid hydride, P_2H, in the presence of little water. When BPI_2 is heated in an atmosphere of hydrogen, boron phosphoiodide, BPI, is formed as a finely divided red powder which is somewhat less hygroscopic then BPI_2. This compound, BPI, volatilizes in a vacuum at 210–250°C. without melting and condenses as orange-yellow crystals. Strong oxidizing acids decompose BPI with the formation of iodine.

Although several aluminum phosphides have been reported,[78] recent investigations[101] indicate that there is only one aluminum phosphide—the monophosphide, AlP. This compound is made by passing phosphorus vapor in a stream of hydrogen over hot aluminum. Pure aluminum phosphide is insoluble in both cold and boiling water but dissolves in dilute hydrochloric acid with the evolution of phosphine. This reaction is one of the best procedures for the preparation of pure phosphine. Hot concentrated oxidizing acids have little effect on AlP, but hot concentrated alkalies liberate phosphine. When aluminum phosphide is subjected to dry hydrogen chloride vapor, the solid phosphorus hydride, P_2H, is formed. At very high temperatures, phosphorus is lost from aluminum phosphide; but vapor pressure data are not available. Heating AlP in air converts it to alumina and aluminum phosphate, $AlPO_4$—apparently some phosphorus is lost as PH_3.

Gallium and indium phosphides, GaP and InP, are quite similar[102] to

[101] W. E. White and A. H. Bushey, *J. Am. Chem. Soc.*, **66**, 1666 (1944); E. Montignie, *Bull. soc. chim.*, **1949**, 276.

[102] H. Welker, *Z. Naturforsch.*, **7a**, 744 (1952); *ibid.*, **8a**, 248 (1953).

aluminum phosphide, AlP. These compounds are prepared by heating the elements in stoichiometric proportions in a vacuum. The reaction is slow, and the temperature must be raised to 700°C. to complete it. Unlike aluminum phosphide, the phosphides of gallium and indium dissolve with difficulty in dilute hydrochloric acid. The crystal structures of AlP, GaP, and InP are similar. All of them exhibit a zinc-blend type of structure,[102,103] in which both component elements have four-fold coordination. These compounds are isoelectronic with the elements of Group IVA. In other words, AlP should be very similar to elemental silicon. Thus, in silicon the

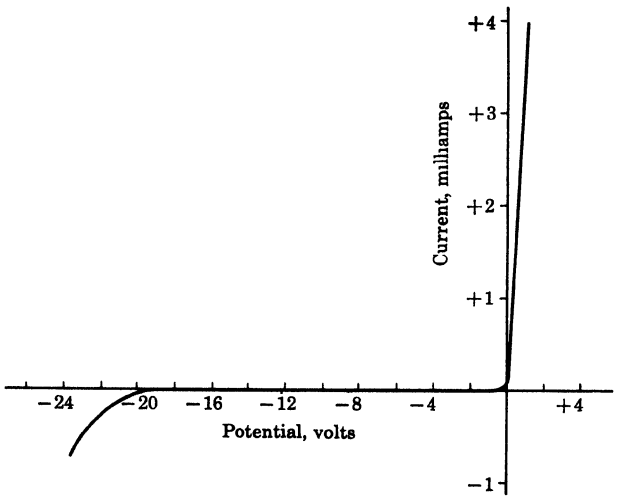


Fig. 4-12. Rectifier curve of a *p*-conducting crystal of indium phosphide, InP, obtained with point contacts.

individual atoms also exhibit four-fold coordination, and the Si-Si distance is 2.346 A., as compared to an Al-P distance of 2.35 A. in aluminum phosphide. Moreover, in aluminum phosphide, the Al-Al distance is 3.84 A. as compared to 2.858 A. in metallic aluminum. This means that the aluminum atoms, as well as the phosphorus atoms, are distantly separated from like atoms so that there should be essentially no metallic bonding. Like the unreacted elements in Group IVA of the periodic table, the phosphides of the Group IIIA elements are three-dimensional polymers. In these phosphides—as exemplified by AlP—both atoms have an octet of electrons[104] and exhibit an sp^3-type of hybridization.

[103] L. Passerini, *Gazz. chim. ital.*, **58**, 655 (1928); V. Goldschmidt, *Geochem. Vert.*, **8**, 197 (1927); also see ref. 97.

[104] L. Pauling, *Proc. Natl. Acad. Sci. U.S.*, **36**, 533 (1950).

As in the case of the elements of Group IVA, the phosphides of aluminum, gallium, and indium can act as either *p* or *n* semiconductors,[102,105] depending on the kind and level of the impurities. A plot[102] of current *versus* applied potential is given for a *p*-conducting crystal of indium phosphide in Figure 4-12. This curve shows the rectifying characteristics of the crystal. Indium phosphide has also been shown to exhibit transistor properties.[102]

Although the earlier literature[78] claims that thallium phosphides do not exist, a phase study[106] indicates the presence of TlP_3 which melts at about 420°C. This substance tends to dissociate into its constituents at all temperatures, so that a high pressure is necessary for its formation. Another thallium phosphide, Tl_3P, has been reported.[107] It was prepared by heating theoretical amounts of thallium and white phosphorus in a sealed tube at 400°C. Proof that this is a definite compound is lacking.

Phosphides of Group IVA Elements

The best-known carbon-phosphorus compound is the high-temperature molecule, CP, which is known from its band spectrum.[108] The only reference[109] to a phosphorus carbide stable at room temperature is to a reaction product of phosphorus trichloride with acetylene magnesium iodide, IMgC≡CMgI. This Grignard reaction product is a yellowish white amorphous precipitate, having the empirical formula PC_3, which was found to be insoluble in ordinary solvents and not attacked by acids or alkalies.

Although no silicon phosphides appear in the older literature,[78] a silicon phosphide having the formula SiP has been demonstrated to exist by vapor pressure studies.[110] This silicon phosphide decomposes according to the following reaction:

$$4\,SiP(s) \longrightarrow 4\,Si(s) + P_4(g) \qquad (4\text{-}33)$$

In the temperature range of 1000-1200°C., the partial pressure of P_4 corresponding to this decomposition is given by the following equation from which a heat of reaction, ΔH, of 72 kcal. was calculated.

$$\log p_{mm.} = -15{,}710/T + 13.769 \qquad (4\text{-}34)$$

[105] T. Witmer, *Crystal Rectifiers*, McGraw-Hill Book Co., Inc., New York, 1948, p. 67.

[106] Q. A. Mansuri, *J. Chem. Soc.*, **1927**, 2993.

[107] E. Montignie, *Bull. soc. chim.*, **4**, No. 5, 295 (1937).

[108] H. Barwald, G. Herzberg, and L. Herzberg, *Ann. Phys.*, **20**, 569 (1934). For more recent discussions, see G. Lovera, *Nuovo cimento*, **9**, 541 (1952) and J. W. Linnett, *Trans. Faraday Soc.*, **38**, 1 (1942).

[109] E. de Mahler, *Bull. soc. chim.*, **29**, 1071 (1921).

All of the phosphorus can be removed from silicon phosphide by heating in a vacuum at 1000°C. Although it is not thermally stable, silicon phosphide is resistant to oxidation, even at red heat, due to the formation of a protective coating of silicon dioxide. However, as might be expected, it reacts with chlorine at elevated temperatures. Silicon phosphide does not react appreciably with cold water, but it does decompose in boiling water to form phosphine. Only two-thirds of the total phosphorus is given off as phosphine, so that probably either a lower silicon phosphide or the solid phosphorus hydride, P_2H, is formed in the reaction.

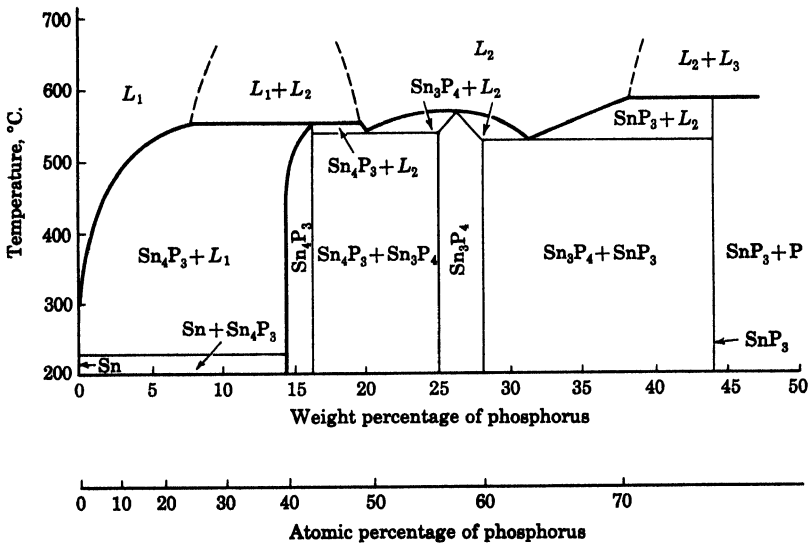


Fig. 4-13. Phase diagram of the tin-phosphorus system.

Although the structure of silicon phosphide has not been determined, it has been shown to have a different x-ray pattern than that of elemental silicon.[110] Silicon phosphide is nonmetallic in character, and the vapor pressure measurements indicate that it is a true compound. A small amount of phosphorus can be dissolved in molten silicon where, upon cooling, it acts as an impurity center with respect to the semiconducting properties of silicon. In this role, phosphorus has been classed as a superior addition agent for silicon,[105] increasing conductivity and producing a good, stable rectifier.

[110] W. Biltz, H. Hartmann, F. W. Wrigge, and F. Wiechmann, *Sitzber. preuss. Akad. Wiss., Physik.-math. Kl.*, **7**, 99 (1938).

Germanium phosphide, GeP, has been made by heating metallic germanium with an excess of phosphorus to temperatures of 400°C. or more in an evacuated tube.[111] X-ray analysis, as well as vapor pressure measurements, show that the reaction product has the formula GeP and is distinct from both elemental germanium and elemental phosphorus. The heat of formation of germanium phosphide from solid germanium and P_4 gas is −37 kcal.

Unlike the phosphides of silicon and germanium, which are probably three-dimensional polymers somewhat similar to the phosphides of aluminum, gallium, and indium, the phosphides of tin are considerably more metallic in character and appear to be related to the phosphides of the alkali and alkaline earth metals and some of the phosphides of the transition metals. The phase diagram[112] of the tin-phosphorus system is given in Figure 4-13, where it can be seen that there are three phosphides, SnP_3, Sn_3P_4, and Sn_4P_3. In this phase diagram both Sn_4P_3 and Sn_3P_4 appear as limited regions of solid solution, whereas SnP_3 exhibits an exact composition. There are three different liquid phases in the tin-phosphorus system —liquids which have limited solubility in each other. This means that in the regions indicated in Figure 4-13 as $L_1 + L_2$ and $L_2 + L_3$, two immiscible liquid layers of melt are present. In the three-phase system, Fe—Sn—P, which has been examined in detail,[113] no mixed phosphides of iron and tin were observed. The effect of adding either iron or phosphorus to tin is to increase the fusion temperature of the alloy rapidly. When tin is added to the iron-phosphorus system, the latter fusion diagram is unaffected up to about 5% tin, except for a slight lowering (about 70°) of the eutectic temperatures.

When tin is reacted with an excess of phosphorus in a sealed tube, SnP_3 is formed. This phosphide is insoluble in hydrochloric acid and, upon being heated in a vacuum at 350°C., loses phosphorus to form Sn_4P_3, which is soluble in HCl.[114] Sn_4P_3 can be separated from tin in alloys containing up to 13% phosphorus by making the alloy the anode in a solution of sodium polysulfide. This causes the tin to dissolve, leaving silver-white crystals of Sn_4P_3. Presumably, the tin monophosphide, SnP, reported in the literature[114] is identical to the compound Sn_3P_4 shown in Figure 4-13. When this compound is heated to 415°C., it loses phosphorus and forms Sn_4P_3.

[111] M. Zumbusch, M. Heimbrecht, and W. Biltz, *Z. anorg. u. allgem. Chem.*, **242**, 237 (1934).

[112] A. C. Vivian, *Inst. Metals Preprint*, 1920, 35 pp.

[113] R. Vogel and G. Swingmann, *Arch. Eisenhüttenw.*, **26**, 631 (1955).

[114] P. Jolibois, *Compt. rend.*, **150**, 106 (1910); *Proc. Int. Assoc. Testing Materials*, **2**, No. 10, II$_{18}$ (1912).

The vapor pressure of phosphorus over the various tin phosphides has not as yet been measured. It is interesting to note that reduction of tin phosphate with hydrogen at 600°C. gives only metallic tin and no tin phosphides.[115]

Because of the low melting point of the tin phosphides (about 550°C.), the ease of formation of the higher tin phosphides under pressure, and the difference in solubilities of SnP_3 and Sn_4P_3 in hydrochloric acid, these compounds can be used in preparing phosphides of other metals. In general, the process is to bring to red heat in an enclosed system a mixture of red phosphorus with a 5% alloy of the desired metal in tin Any SnP_3 which is formed can be converted to Sn_4P_3 by heating in a vacuum at 350°C. This latter tin phosphide can then be dissolved in hydrochloric acid to leave the phosphide of the desired metal. Nickel, cobalt, and platinum phosphides have been prepared in this way.[116,117]

Molten lead will dissolve up to about 1.5% of phosphorus.[78] Although a lead phosphide of the formula PbP_2 made by reacting white phosphorus and molten lead has been described by several authors,[118] the existence of this compound is considered questionable, since in another study[119] phosphorus and lead were not found to react in elemental form. By combining lead acetate dissolved in ethyl alcohol with phosphine dissolved in alcoholic potassium hydroxide, a black flocculent precipitate having the formula Pb_3P_2 is formed This precipitate is very unstable and, on standing, decomposes to leave a film of lead on the glass walls of the containing vessel Water and dilute acids or alkalies react slowly with this product when cold, and rapidly when warm, to give phosphine.

By allowing phosphorus to react with the lead alloys of zinc, cadmium, or mercury for 8–10 days at temperatures ranging from 525 to 610°C., there are produced[120] ternary phosphides exhibiting the general formula $MPbP_{14}$, where M stands for Zn, Cd, or Hg. These compounds all have similar properties. They are stable in air and do not dissolve in water or nonoxidizing mineral acids. These phosphides are all well crystallized and exhibit a grey to silver color, being opaque and having a metallic luster. However,

[115] J. C. Hutter, *Ann. chim.* (*Paris*), **8**, 450 (1953).

[116] W. Biltz and M. Heimbrecht, *Z. anorg. u. allgem. Chem.*, **237**, 132 (1938)

[117] W. Biltz, I. Mathieson, and F. W. Wrigge, *Z. anorg. u. allgem. Chem.*, **232**, 284 (1937).

[118] A. C. Vournasos, *Ber.*, **44**, 3269 (1911); A. Stock and F. Golmolka, *ibid.*, **42**, 4510 (1909); G. Linck and P. Moller, *ibid.*, **41**, 1404 (1908).

[119] A. Granger, *Ann. chim. Phys.* **14**, No. 7, 74 (1898); *Contribution à l'étude des phosphures métalliques*, Thesis, Univ. of Paris, 1898; *Compt. rend.*, **124**, 190 (1897).

[120] H. Krebs, I. Pakulla, and G. Zurn, *Z. anorg. u. allgem. Chem.*, **278**, 284 (1955).

they do not conduct electricity and have very weak piezoelectric properties. The crystals belong to the tetragonal system and show fibrous cleavage along the *c*-axis. The dimensions of the unit cells of the mercury and cadmium compounds, $HgPbP_{14}$ and $CdPbP_{24}$, are the same, whereas the cell constants of the zinc compound, $ZnPbP_{14}$, are several per cent smaller. From a partial analysis of the x-ray data and the fact that the crystals exhibit fibrous cleavage and contain a large amount of phosphorus, it has been suggested that the structure involves straight chains of interconnected phosphorus atoms directed along the *c*-axis.[120] If this is so, these compounds represent the unusual case of a phosphide in which the phosphorus atoms are not widely separated from each other. In other words, Krebs *et al.* suggest that these compounds are true polyphosphides Another item of note concerning the compound $HgPbP_{14}$ is that it is stable, although binary compounds of phosphorus with either lead or mercury may not exist or, at least, are difficult to prepare and store.

Phosphides of Arsenic, Antimony, and Bismuth

X-ray and thermal analysis studies[121] show that phosphorus forms only one compound with arsenic, arsenic monophosphide, AsP. This compound, AsP, consists of black leaflets which have the superficial appearance of graphite. Its specific electrical resistance is in the range of 1–10 ohms, only a little higher than that of black phosphorus. Presumably, this compound has a structure similar to those of black phosphorus and grey arsenic. In grey arsenic, the atoms are arranged in the same way as in black phosphorus so that the crystal consists of layers in which each arsenic atom has three equidistant nearest-neighbor arsenic atoms at 2.51 A. and then three more neighbors somewhat farther removed.

According to a recent phase diagram study,[122] there are no antimony phosphides. The greatest solubility of phosphorus in molten antimony is 0.85%, which causes a reduction in melting point of the antimony from 630.5 to 612°C.

There also does not seem to be a bismuth phosphide, although there were a few reports of such a substance in the early literature.[78] By passing phosphine into a solution of bismuth trichloride in ether, a black, hygroscopic deposit having the composition PBi_3Br_7 is formed.[123]

[121] W. Klemm and I. von Falkowski, *Z. anorg. Chem.*, **256**, 343 (1948).

[122] R Vogel and D. Horstmann, *Arch Eisenhuttenw.*, **23**, 127 (1952).

[123] A Cavazzi and D. Tivoli, *Gazz. chim ital.*, **21**, 306 (1891). Also see A. Cavazzi, *ibid.*, **14**, 219 (1884).

Phosphides of Copper, Silver, and Gold

The well-recognized phosphides of copper, silver, and gold are tabulated below.

	CuP_2		Cu_3P_2	Cu_2P	Cu_3P
AgP_3	AgP_2				Ag_3P
		Au_2P_3			Au_3P

The two best established copper phosphides are CuP_2 and Cu_3P. Metallic copper reacts with phosphorus vapor at high temperatures and pressures to form CuP_2. This compound then decomposes to form Cu_3P according to the following equation.

$$^{12}/_{5}\ CuP_2(s) \longrightarrow {}^{4}/_{5}\ Cu_3P(s) + P_4(g) \qquad (4\text{-}35)$$

In the temperature range from 600 to 800°C., the partial pressure[80,124] of phosphorus vapor, P_4, corresponding to equation 4-35 is given below. At 760°C. the vapor pressure of phosphorus over Cu_3P is immeasurably small. For the following equation, the heat of reaction, ΔH, is 52 kcal.

$$\log p_{mm} = -11{,}370/T + 13.827 \qquad (4\text{-}36)$$

According to this equation, the partial pressure of phosphorus over a mixture of CuP_2 and Cu_3P is 1 atm. at 765°C. Both CuP_2 and Cu_3P have been observed in a thermal analysis of the copper-phosphorus system.[125] These compounds have also been made by reduction of heated copper metaphosphate by hydrogen.[115] The lower phosphide, Cu_3P, has been prepared by electrolysis[126] of sodium phosphate melts containing copper oxide and by the reaction of excess phosphine on solutions of copper sulfide.[127]

The phase diagram of the copper-phosphorus system has been determined[125,127] up to 15% copper, as shown in Figure 4-14. Beyond 14% copper, corresponding to the phosphide Cu_3P, there is an eutectic between Cu_3P and another higher phosphide. At the left side of the phase diagram, it should be noted that phosphorus dissolves in metallic copper. The maximum solubility of phosphorus in copper is 1.7% at a temperature of 714°C. An x-ray study[128] has been carried out on Cu_3P, and the results are reported in Table 4-4. In this compound, the phosphorus atoms have eight nearest-neighbor copper atoms at 2.3–2.5 A. plus four more at 3.2–3.7 A. The dis-

[124] H. Haraldsen, *Z. anorg. u. allgem. Chem.*, **240**, 337 (1939).
[125] E. Kreutzer, *Z. Physik*, **48**, 556 (1928).
[126] M. Chêne, *Compt. rend.*, **214**, 977 (1924).
[127] E. Heym and O. Bauer, *Z. anorg. Chem.*, **52**, 129 (1907); D. K. Crampton, H. L. Burghoff, and J. T. Stacy, *Trans. Am. Inst. Mining Met. Engrs.*, **137**, 354 (1940).
[128] B. Steenberg, *Arkiv Kemi Mineral. Geol.*, **12A**, 1 (1938).

tance of closest approach for the copper atoms to the six nearest copper atoms ranges from 2.54 to 2.64 A., depending on the position of the copper in the lattice. These values should be compared to the Cu-Cu distance of 2.55 A. in metallic copper. Cu_3P possesses a metallic luster, conducts electricity, and is brittle and dense. It is feebly attacked by hydrochloric acid and readily oxidized by air.

The compound Cu_2P has been reported to be obtained by electrolysis of a fused phosphate containing copper oxide.[126] Upon heating, Cu_2P decomposes to form Cu_3P, as would be expected. Since Mn_2P, Fe_2P, and

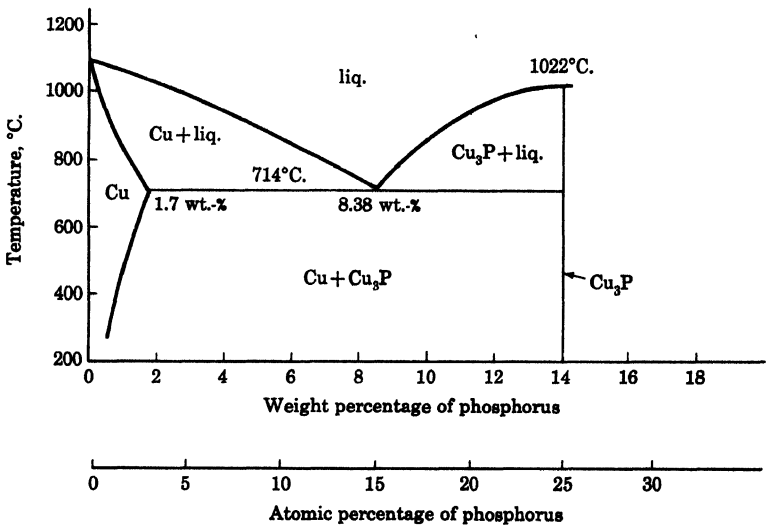


Fig. 4-14. Phase diagram of the copper-rich end of the copper-phosphorus system.

Ni_2P all exist and are isomorphous, it might be expected that Cu_2P would also belong to this isomorphous series. X-ray examination of this compound would help to prove its existence. The compound Cu_3P_2 is said to be formed[78,83] as an intermediate product in the reaction of phosphine with copper salts, either as solids or in solution. In view of the fact that zinc and cadmium form similar compounds, its existence does not seem unlikely. The reactions of phosphine with cupric salts should definitely be reinvestigated. It would also be of interest to study the reactions of cuprous salts with phosphine. In addition to the copper phosphides described here, the earlier literature[78] also refers to a Cu_5P_2 and a CuP.

Because of their use in phosphor bronzes, copper-phosphorus alloys and

copper phosphides are made on a commercial scale. The phase diagrams involving phosphorus, copper, and other metals have been studied to some extent. Thus, the Cu—Sn—P system has had a great deal of work done on it.[129] In addition, studies have also been carried out on the following systems: Cu—Fe—P,[130] Cu—Ni—P,[131] Cu—Mn—P,[131] Cu—Cr—P,[131] Cu—Ag—P,[132] Cu—Zn—P,[133] and Cu—Si—P.[133] Because of the use of phosphorus in deoxidizing copper and the interest of metallurgists in the reactions between metals and slags, several diverse investigations have also been carried out on the system Cu—P—O.[134]

The silver-phosphorus system has been examined[132] by thermal analysis up to only a few per cent phosphorus. An eutectic occurs at a phosphorus content of about 0.98% by weight and a temperature of 878°C. The maximum solubility of phosphorus in silver is 1.4% at 960°C. As would be expected, the two silver phosphides which contain the most phosphorus exhibit relatively high partial pressures of phosphorus. In the case of the silver phosphides, there is the stepwise decomposition shown in the following equations:

$$4\,AgP_4(s) \longrightarrow 4\,AgP_2(s) + P_4(g) \qquad (4\text{-}37)$$

$$2\,AgP_2(s) \longrightarrow 2\,Ag(s) + P_4(g) \qquad (4\text{-}38)$$

The partial pressures[80,135] of phosphorus as P_4 over AgP_3 and AgP_2, respectively, are given by the following equations, which apply to the temperature range from 400 to about 550°C. According to these equations, the temperature at which the partial pressure of P_4 vapor is 1 atm. is 515°C. for AgP_3 and 551°C. for AgP_2.

$$\log p_{mm.} = -7759/T + 12.726 \qquad \Delta H = 35.5 \text{ kcal} \qquad (4\text{-}39)$$

$$\log p_{mm} = -7161/T + 11.566 \qquad \Delta H = 32.7 \text{ kcal.} \qquad (4\text{-}40)$$

[129] J. Vero, *Z. anorg. u. allgem. Chem.*, **213**, 257 (1933), L C. Glaser and H. J. Seemann, *Z. tech. Physik*, **7**, 42 (1926); M. Levi-Malvano and F. S. Orofino, *Gazz chim. ital.*, **41**, II, 297 (1912); D. W. D. Showell, *J. Inst. Metals*, **76**, 527 (1950); L. Guillet, *Cuivre et laiton*, **5**, 529 (1932); L. C. Glaser and H. J. Seemann, *Z. tech. Physik*, **7**, 90 (1926); N. H. Polakowski, *J. Inst. Metals*, **81**, 617 (1953).

[130] R. Vogel and J. Berak, *Arch. Eisenhuttenw*, **21**, 327 (1950); E. Crepaz, *Atti e mem. acad. sci. Padova, Classe sci. fis. mat.* [*N.S*], **52**, 91 (1936); also see ref. 123.

[131] H. Nowotny and E. Henglein, *Monatsh.*, **79**, 385 (1948).

[132] H. Moser, K. W. Fröhlich, and E. Raub, *Z. anorg. u. allgem. Chem.*, **208**, 325 (1932); K. W. Frohlich, *Mitt. Forsch.-Insts. u. Probieramt Edelmetalle*, **6**, 69 (1932).

[133] W. E. Lindlief, *Metals & alloys*, **4**, 85(1933).

[134] W. Krings, *Z. Metallkunde*, **26**, 247 (1934); W. Oelsen, *Z. Erzbergbau u. Metallhuttenw.*, **2**, 328, 368 (1949); B. T. Houlden and W. A. Baker, *Metallurgia*, **47**, 223 (1953).

[135] H. Haraldsen and W. Biltz, *Z. Elektrochem.*, **37**, 502 (1931)

In the similar manner, the gold phosphide, Au_2P_3, loses phosphorus to form Au_3P. The equations for this reaction and for the corresponding pressure[80] of phosphorus vapor, P_4, in the temperature range of 550–700°C. are given below. The heat of the decomposition reaction for Au_2P_3 is 41.7 kcal.

$$^4/_3\ Au_2P_3(s) \longrightarrow {}^8/_3\ Au(s) + P_4(g) \qquad (4\text{-}41)$$

$$\log p_{mm} = -9126/T + 12.210 \qquad (4\text{-}42)$$

At 705°C., the pressure of P_4 vapor over Au_2P_3 is 1 atm.

With respect to their chemical properties, the silver and gold phosphides are quite similar to the copper phosphides. As is the case with copper salts, solutions of silver or gold salts are found to react with phosphine. In the reaction with silver nitrate, a compound having the composition $Ag_3P \cdot 3AgNO_3$ is first formed[136] as an unstable yellow intermediate. This compound decomposes to give a precipitate of Ag_3P which, in dilute solution, further decomposes into silver and the lower oxyacids of phosphorus. Depending on the concentration, a number of different products can be obtained from the action of phosphine on solutions of silver nitrate. Among these products are the silver nitratophosphide, $Ag_3P \cdot 3AgNO_3$; the silver phosphide, Ag_3P; nitrogen tetroxide, metallic silver; and various oxyacids of phosphorus. Phosphine will react with a large excess of silver salts in water to give a stoichiometric yield of phosphoric acid and metallic silver.[83,110] The same thing is true of auric salts.[137] In the case of the gold salts, the reaction with phosphine usually causes a reduction of the gold to metallic form. However, it is possible to make auric phosphides from phosphine in water.[137]

Phosphides of Zinc, Cadmium, and Mercury

Both zinc and cadmium form two phosphides,[95,103,114,138] ZnP_2 and Zn_3P_2 for zinc and CdP_2 and Cd_3P_2 for cadmium. The orange-red diphosphides are formed by heating the elements in a sealed tube at red heat. They melt at temperatures in the neighborhood of 700°C. and can be sublimed at this temperature in an atmosphere of phosphorus vapor. However, when heated in a vacuum at 700°C., they decompose to form the lower stable phosphides, M_3P_2. The diphosphides do not react with water. With acids

[136] T. Poleck and K. Thümmel, *Ber.*, **16**, 2435 (1883); *Arch. Pharm.* **22**, No. 3, 1 (1884). Also see J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1923, Vol. III, pp. 470–71.

[137] A. Baker and F. L. Usher, *Trans. Faraday Soc.*, **36**, 385 (1940).

[138] M. von Stackelberg and R. Paulus, *Z. physik. Chem.*, **B28**, 427 (1935), P. Jolibois, *Compt. rend.*, **147**, 801 (1908)

they react slowly to form phosphine. The sesquiphosphides are also stable in water and in cold nonoxidizing acids. The reaction[83] of phosphine with solutions of zinc or cadmium salts gives the lower phosphide, Zn_3P_2 and Cd_3P_2, respectively. The zinc phosphide has been used as a rodenticide, as a result of which some investigations have been carried out on the toxicity of this material.[139]

The phosphides Zn_3P_2 and Cd_3P_2 crystallize in the tetragonal system with eight formula weights per unit cell.[138] These compounds are iron grey, opaque, and have a metallic luster. They are relatively good conductors of electricity, with the cadmium compound being a better conductor than the zinc. The photoelectric and other semiconducting properties of Zn_3P_2 have been reported in the literature.[140] The diphosphides, ZnP_2 and CdP_2, exhibit a pseudocubic crystal structure which has not been worked out so thoroughly as the structure of the sesquiphosphides.

In Zn_3P_2 and Cd_3P_2, the phosphorus atoms are surrounded by six nearest-neighbor metal atoms, as shown in Table 4-4, and the metal atoms have four nearest-neighbor phosphorus atoms as well as three like atoms at a somewhat larger distance: In Zn_3P_2, the Zn-Zn distances are 3.00 and 3.07 A., as compared to 2.66 and 2.91 A. in metallic zinc. Likewise, in Cd_3P_2, the Cd-Cd distances are 3.22 and 3.33 A., as compared to 2.97 and 3.29 A. in the metal. As is usually the case with the phosphides, the phosphorus atoms are well separated (eight nearest neighbors at 4.0 A.). See Table 4-4 for further details concerning these structures.

Mercury phosphides have not as yet been studied by the methods of physical chemistry. Although there is a report[118] of the formation of a mercury phosphide by heating mercury and phosphorus under a layer of paraffin, mercury phosphides have generally not been obtained from a reaction involving the elements. The reaction between phosphine and solutions of mercurous or mercuric salts gives black precipitates containing phosphorus and mercury. The preparation of Hg_3P_2 by this procedure has been reported.[83] There is also a mixed compound which can be written either as $3HgCl_2 \cdot Hg_3P_2$[83] or as $P(HgCl)_3$.[101] Other complex phosphides have been reported.[78] In view of the ease with which mercury forms complex compounds with ammonia, it is not surprising to find that similar compounds are produced with phosphine. The reactions between phos-

[139] K. Becker and G. A. Hunold, *Pharmazie*, **3**, 543 (1948); J. W. Elmore and F. J. Roth, *J. Assoc. Offic. Agr. Chemists*, **26**, 559 (1943); G. Dello Iojo, *Folia Med. (Naples)*, **32**, 156 (1949).

[140] J. Lagrenaudie, *J. chim. phys.*, **50**, 545 (1953).

phine and mercury salts should be reinvestigated, using modern techniques of structure analysis.

Phosphides of Rare Earth and Actinide Metals

Lanthanum, cerium, praseodymium, and neodymium react[141] with phosphorus (violently in the temperature range of 400–500°C.) to form the normal phosphides, MP. With respect to air oxidation, CeP is the most stable, as it can be heated in the open with only slight oxidation. PrP oxidizes slowly in air, whereas LaP is rapidly oxidized. All of these phosphides react with water to liberate phosphine. These rare earth phosphides exhibit a cubic structure of the sodium chloride type, in which both the rare earth and phosphorus atoms have a coordination number of six.[141] The internuclear distances observed in these structures are La-P = 3.01 A., Ce-P = 2.95 A., Pr-P = 2.93 A., and Nd-P = 2.91 A.

Apparently the actinide series of elements most readily forms two types of compounds; M_3P_4 and MP. The known phosphides of this series of compounds are Th_3P_4,[142] ThP,[143] U_3P_4,[144] UP,[144] Np_3P_4,[145] and perhaps U_2P_3.[146] All of these phosphides, with the exception of U_2P_3, are prepared by reaction between the elements, usually under pressure. The U_2P_3 composition was made by passing UH_3 and PH_3 together through a heated tube.

The usual phosphides of the actinide metals—M_3P_4 and MP—exhibit cubic crystal structures. X-ray data on the uranium and thorium phosphides of these compositions have been reported.[143,147] A detailed structure analysis of the Th_3P_4 is presented in Table 4-4. The phosphides, M_3P_4 and MP, exhibit a greyish black color and have a metallic luster. They do not react with water. However, Th_3P_4 and U_3P_4 decompose in cold solutions of hydrochloric acid to liberate phosphine.

In the crystals of Th_3P_4, each thorium atom has eight nearest-neighbor phosphorus atoms at 2.98 A. and eight thorium atoms at 4.02 A. In thorium metal, the Th-Th distance is 11% shorter, being 3.59 A. This expansion of the metal-to-metal distance is typical[74] of the interstitial com-

[141] A. Iandelli and E. Botta, *Atti accad. nazl. Lincei, Mem., Classe sci. fis., mat. e nat.*, **24**, 459 (1936); *ibid.*, **26**, 233 (1937); *Gazz. chim. ital.*, **67**, 638 (1937).

[142] E. F. Strotzer, W. Biltz, and K. Meisel, *Z. anorg. u. allgem. Chem.*, **238**, 69 (1938).

[143] K. Meisel, *Z. anorg. u. allgem. Chem.*, **240**, 300 (1939).

[144] H. Heimbrecht, M. Zumbusch, and W. Biltz, *Z. anorg. u. allgem. Chem.*, **245**, 391 (1941).

[145] I. Sheft and S. Fried, *J. Am. Chem. Soc.*, **75**, 1236 (1953).

[146] A. S. Newton, J. C. Warf, F. H. Spedding, O. Johnson, I. B. Johns, R. W. Nottorf, J. A. Ayres, R. W. Fisher, and A. Kant, *Nucleonics*, **4**, No. 2, 17 (1949).

[147] M. Zumbusch, *Z. anorg. u. allgem. Chem.*, **245**, 402 (1941); *ibid.*, **243**, 322 (1940).

pounds which are also known as the hard metals. The phosphorus atoms in Th_3P_4 have six nearest-neighbor thorium atoms at the Th-P distance of 2.98 A. and five phosphorus atoms at 3.20–3.72 A.

Phosphides of Titanium, Zirconium, Vanadium, Niobium, and Tantalum

The recognized phosphides of the metals in Groups IVB and VB are listed below. It should be noted that there are two kinds of "monophosphides"—the α-forms, which are slightly deficient in phosphorus (*e.g.*, $ZrP_{0.90}$), and the β-forms, which appear to correspond exactly to a monophosphide (*e.g.*, ZrP). Generally speaking, the phosphides listed below all lie in the class of hard metals. Recently, the monophosphides in this class have been carefully studied[148] by x-ray; and structural data concerning them are given in Table 4-4.

	β-MP	α-MP			
TiP_2		$TiP_{0.95}$		Ti_2P(?)	
ZrP_2	ZrP	$ZrP_{0.90}$			Zr_3P
VP_2	VP		V_3P_2	V_2P	V_3P
NbP_2	NbP	$NbP_{0.95}$			
TaP_2	TaP	$TaP_{0.95}$			

The diphosphides, MP_2, can be made by heating the metal in a sealed tube with an excess of phosphorus,[81,148] or by passing phosphine over the metal at elevated temperatures.[51] It is very likely that Ti_2P is really Ti_3P since Shönberg showed that it has the Fe_3P structure. Some work has been reported on reacting phosphine and the metal chloride by passing these gases through a hot tube to give either the mono- or diphosphide.[149] When titanium tetrachloride is treated in the cold with phosphine, it forms a yellow crystalline substance which, when heated, decomposes to give phosphine, hydrogen chloride, and some titanium monophosphide, TiP.

The diphosphides decompose to give the monophosphide plus phosphorus vapor according to the following equation.

$$4\ MP_2(s) \longrightarrow 4\ MP(s) + P_4(g) \qquad (4\text{-}43)$$

The partial pressures corresponding to this decomposition have been measured for ZrP_2,[150] VP_2,[81] NbP_2,[151] and TaP_2.[152] The temperatures at which the vapor pressure of phosphorus is 1 atm. are 891°C. for ZrP_2, 711°C.

[148] N. Shönberg, *Acta Chem. Scand.*, **8**, 226 (1954).

[149] J. Gewecke, *Ann.*, **361**, 79 (1908).

[150] E. F. Strotzer, W. Biltz, and K. Meisel, *Z. anorg. u. allgem. Chem.*, **239**, 216 (1938).

[151] A. Reinecke, W. Wiechmann, M. Zumbusch, and W. Biltz, *Z. anorg. u. allgem. Chem.*, **249**, 14 (1942).

[152] M. Zumbusch and W. Biltz, *Z. anorg. u. allgem. Chem.*, **246**, 35 (1941).

for VP_2, and 864°C. for TaP_2. The heats of these reactions, ΔH, are 48 kcal., 56 kcal., and 60 kcal., respectively. The equations for the partial pressure of phosphorus vapor as a function of temperature over a mixture of the diphosphide and the monophosphide are given below:

For ZrP_2

$$\log p_{\text{mm.}} = -10{,}600/T + 11.984 \tag{4-44}$$

For VP_2

$$\log p_{\text{mm.}} = -12{,}200/T + 15.281 \tag{4-45}$$

For TaP_2

$$\log p_{\text{mm}} = -13{,}160/T + 14.453 \tag{4-46}$$

It is obvious from the above vapor pressure data that a good way to make the monophosphide of these elements is to heat the diphosphide in a vacuum, and this method of preparation has been employed. Depending on the temperature at which the heating is carried out, the α- or β-form of the monophosphide is obtained. Both the α- and β-forms exhibit no measurable vapor pressure of phosphorus at temperatures around 1000°C. The lower phosphides can be prepared directly from the elements.[150] For titanium, the best-known phosphide is the monophosphide, which has been discussed by a number of investigators.[78,153] The other two titanium phosphides have been described only briefly.

A considerable amount of work[85,154] has been done on the preparation of vanadium phosphides, VP and V_2P, by electrolysis of metaphosphate melts containing V_2O_5. The phosphides, NbP and TaP, have also been prepared by this procedure.[154]

The structures of the monophosphides of the Group IVB and VB metals can be classified into four types. One type-group is made up of both the α- and β-forms of NbP and TaP. These four similar structures consist of two-dimensional layers of metal and phosphorus atoms in which both kinds of atoms are surrounded by four atoms of the opposite kind. As is the usual case with the known phosphides, the P-P distances are sufficiently large so that the phosphorus atoms are well isolated from each other. The metal-to-metal distances, both within a layer and between layers, are about 15%

[153] W. Biltz, A. Rink, and F. Wiechmann, *Z. anorg. u. allgem. Chem.*, **238**, 395 (1938)

[154] H. Hartmann and W. Mässing, *Z. anorg. Chem.*, **266**, 98 (1951); M. Chene, *Compt rend.*, **208**, 1144 (1939).

greater than in the pure metals. Presumably, the separate layers are bound together by the same forces which hold metals together.

The three other structure types are represented by (1) TiP and β-ZrP, (2) VP, and (3) α-ZrP. The γ' phase of MoC and Form-I of NbN are isomorphous with TiP and β-ZrP. These structures are typical of the hard metals in that a metal-type lattice is found with the phosphorus atoms in the lattice holes. In TiP and β-ZrP, the mean intermetallic distances are 17% and 14% greater than those observed for the corresponding pure metals. In the isomorphous NbN, the mean intermetallic distance is 6% greater than in the pure metal. Vanadium monophosphide exhibits metal-to-metal distances averaging about 21% larger than in pure vanadium. Although α-ZrP has a sodium chloride type of structure, the metal-to-metal distance is still not very different than in the pure metal, being 17% larger.

Phosphides of Chromium, Molybdenum, Tungsten, Manganese, and Rhenium

The established phosphides of the metals of Group VIB and VIIB are shown below. Except for the fact that triphosphides, MP_3, and the unusual compound W_4P have been reported, this family of phosphides is quite similar to the phosphides of the metals in Groups IVB and VB.

	CrP_2	CrP	$CrP_{0.88}$	Cr_2P	Cr_3P	
	MoP_2	MoP	$MoP_{0.8}$		Mo_3P	
	WP_2	WP		W_2P		W_4P
MnP_3	Mn_2P(?)	MnP	Mn_3P_2	Mn_2P	Mn_3P	
ReP_3	ReP_2	ReP		Re_2P		

Phase diagram studies have been carried out on the chromium-phosphorus[155,156] and manganese-phosphorus[157] systems. In these diagrams the following compounds were found in the composition range studied: Cr_2P, Cr_3P, Mn_3P_2, Mn_2P, and Mn_3P. The systems Cr—Cu—P, Cr—Mn—P, Cr—Fe—P, Cr—Ni—P, Mn—Cu—P, Mn—Fe—P, and Mn—Ni—P have also been investigated.[156] Vapor pressure measurements have been used to demonstrate the existence of a number of phosphides of these particular

[155] R. Vogel and G. W. Kasten, *Arch. Eisenhüttenw.*, **12**, 387 (1939).

[156] H. Nowotny and E. Henglein, *Z. anorg. u. allgem. Chem.*, **239**, 14 (1938); E. Nowotny, *Naturwiss.*, **26**, 631 (1938); also see ref. 132.

[157] J. Berak and T. Heumann, *Z. Metallkunde*, **41**, 19 (1950); for earlier work see W. Biltz, F. Wiechmann, and K. Meisel, *Z. anorg. u. allgem. Chem.*, **234**, 117 (1937); F. Weichmann, *ibid.*, **234**, 130 (1937); S. Zemczuzny and M. Efremow, *ibid.*, **57**, 241 (1908); *J. Russ. Phys.-Chem. Soc.*, **39**, 777 (1908); also see O. Arstad and H. Nowotny, *Z. physik. Chem.*, **B38**, 356 (1937).

transition metals. These vapor pressure data show that the diphosphides of the Group VIB and VIIB metals are very similar to the diphosphides of the Group IVB and VB metals—all of which decompose according to equation 4-43.

The temperatures at which the vapor pressure of phosphorus as P_4 equals 1 atm. are 700°C. for CrP_2, about 990°C. for MoP_2, and about 1080°C. for WP_2. For the molybdenum and tungsten phosphides, it must be remembered that there will be some dissociation of the P_4 vapor into P_2 at temperatures around 1000°C. The heats of the reactions corresponding to the equation 4-43 are 39 kcal. for the decomposition of CrP_2, 54.4 kcal. for MoP_2, and 76 kcal. for WP_2. The equations for the partial pressure of P_4 vapor over these phosphides are given below. For CrP_2 in the temperature range of 600–700°C.[158]

$$\log p_{\text{mm.}} = -\ 6900/T + 9.829 \tag{4-47}$$

For MoP_2 in the temperature range of 800–1000°C.[158,159]

$$\log p_{\text{mm.}} = -\ 11{,}900/T + 12.287 \tag{4-48}$$

For WP_2 in the temperature range near 1000°C.[159]

$$\log p_{\text{mm.}} = -\ 16{,}700/T + 15.210 \tag{4-49}$$

Manganese triphosphide loses phosphorus to form manganese monophosphides according to the following equation:[159]

$$2\ MnP_3(s) \longrightarrow 2\ MnP(s) + P_4(g) \tag{4-50}$$

At 710°C. the vapor pressure of phosphorus over MnP_3 equals 1 atm., and the heat of the reaction described in equation 4-50 is 54.2 kcal. The partial pressure of P_4 vapor over MnP_3 in the temperature range of 600–700°C. is given by equation 4-51.

$$\log p_{\text{mm.}} = -\ 11{,}860/T + 14.948 \tag{4-51}$$

The rhenium phosphides exhibit stepwise decompositions, all having measurable vapor pressures.[160] These decompositions are given below, along with the pertinent vapor pressure equations.

$$4\ ReP_3(s) \longrightarrow 4\ ReP_2(s) + P_4(g) \tag{4-52}$$

$$\log p_{\text{mm.}} = -\ 17{,}060/T + 16.77 \tag{4-53}$$

[158] F. E. Faller and W. Biltz, *Z. anorg. u. allgem. Chem.*, **248**, 216 (1941).

[159] F. E. Faller, W. Biltz, K. Meisel, and M. Zumbusch, *Z. anorg. u. allgem. Chem.*, **248**, 209 (1941).

[160] H. Haraldsen, *Z. anorg. u. allgem. Chem.*, **221**, 397 (1935).

$$4\,ReP_2(s) \longrightarrow 4\,ReP(s) + P_4(g) \tag{4-54}$$

$$\log p_{mm.} = -\,14{,}220/T + 13.37 \tag{4-55}$$

$$4\,ReP(s) \longrightarrow 2\,Re_2P + P_2(g) \tag{4-56}$$

$$\log p_{mm.} = -\,13{,}780/T + 10.90 \tag{4-57}$$

The diphosphides can all be prepared[151,159–162] by heating the metal with excess phosphorus under pressure at high temperatures. Tungsten diphosphide has also been made by reacting WCl_6 with phosphine.[127,162] All of the lower phosphides of chromium and molybdenum, as well as the monophosphides of tungsten and manganese, can be prepared by heating the diphosphides in a vacuum at appropriate temperatures. Details of these experiments can be found in the papers by Biltz *et al.*[158,159,162] These authors found that, in the tungsten system, W_2P, and W_4P could not be prepared thermally. Similar results were found in a study of the ternary system Fe—W—P.[163] On the other hand, W_3P and W_2P were formed[84,164] on a graphite cathode during the electrolysis at 500°C. of sodium and lithium metaphosphates containing tungsten oxide. The compound W_4P is amorphous and undergoes irreversible decomposition at temperatures in the range of 550°C. or higher to form W_2P and α-tungsten. It is believed that W_4P is not directly precipitated on the cathode but owes its formation to the action of the phosphine-hydrogen mixture produced at the cathode. It is interesting to note that chromium forms[165] a carbide, $Cr_{23}C_6$, which is very close in its metal-to-phosphorus ratio to W_4P.

Electrolysis of fused sodium phosphates containing the appropriate metal oxide has also been used to prepare phosphides in this group of compounds.[84,85] As previously stated, W_2P and W_4P are made by this procedure. In addition, CrP, Mo_3P, MoP, WP, Mn_2P, and MnP have been obtained from electrolysis.

Considerable work[166] has been done on the magnetic properties of MnP and MnP_2, which exhibit ferromagnetism as do the boron, antimony, and

[161] S. Helpert and T. Dickmann, *Ber.*, **47**, 780 (1928).

[162] E. Heinerth and W. Biltz, *Z. anorg. u. allgem. chem.*, **198**, 181 (1931).

[163] R. Schneider and R. Vogel, *Arch. Eisenhüttenw.*, **26**, 483 (1955).

[164] H. Hartmann and J. Orban, *Z. anorg. u. allgem. Chem.*, **226**, 257 (1936); H. Hartmann, F. Ebert, and O. Bretschneider, *ibid.*, **198**, 116 (1931).

[165] A. F. Westgren, *Farnkontorets Ann.*, **117**, 501 (1933).

[166] G. Foex, *Bull. soc. chim. France*, **1949**, 157; C. Guillaud, *Compt. rend.*, **223**, 110 (1946); A. Smits, H. Gerding, and F. Vermast, *Rec. trav. chim.*, **51**, 1178 (1932); R. Forrer, *Compt. rend.*, **194**, 697 (1932); L. F. Bates, *Phil. Mag.* **8**, No. 7, 714 (1929); S. Hilpert and Th. Dieckmann, *Ber*, **47**, 780 (1914); *ibid.*, **44**, 2831 (1912), E. Wedekind, *ibid.*, **40**, 1259 (1907).

arsenic compounds of manganese. The lower Curie point for MnP_2 lies at 38°C., whereas that for MnP is at 28°C. Throughout the paramagnetic region of temperature, MnP follows the Weiss law and does not exhibit any signs of temperature hysteresis, such as is found with MnAs. As predicted from the Weiss theory, there is a small increase in specific heat at the Curie point.[167] In the paramagnetic state, MnP has a magnetic moment of about 1.4 magnetons which is interpreted to mean that the manganese atoms have each gained an average of one electron from the phosphorus atoms. Measurements of the magnetic moments of the paramagnetic nitrides, phosphides, and arsenides usually show no gain or loss of electrons for the metal atom in the compound as compared to being in the pure metal.

All of the phosphides of chromium, molybdenum, and tungsten are grey-black and exhibit a metallic luster. They conduct electricity and are very inert chemically, *i.e.*, they dissolve with considerable difficulty in oxidizing acids. However, the phosphides of the metals of Group VIB are somewhat less thermodynamically stable (based on heats of formation) than those of the Group IVB and VB metals. This corresponds to the behavior of the nitrides of these metals.[168] The detailed atomic structures of the monophosphides of chromium, molybdenum, tungsten, and manganese have been determined and are reported in Table 4-1. In addition, crystallographic studies on Cr_3P and Mo_3P have shown that these compounds are isomorphous with schreibersite, Fe_3P.

Phosphides of Iron, Cobalt, and Nickel

The phosphides of iron, cobalt, and nickel have probably been more extensively studied than those of any of the other metals. A listing of the accepted phosphides of these metals is given below.

	FeP_2	FeP		Fe_2P		Fe_3P
CoP_3		CoP		Co_2P		Co_3P^a
NiP_3	NiP_2	Ni_5P_6(?)	Ni_6P_5	Ni_2P	Ni_5P_2	Ni_3P

[a] Only in solid solution with Ni_3P, Fe_3P, etc.

Phase-diagram studies have been carried out on all three of these groups of phosphides. In the iron-phosphorus system,[169] which is shown in Figure

[167] B. G. Whitmore, *Phil. Mag.* **7**, No. 7, 125 (1929).

[168] I. E. Campbell, Ed., *High-Temperature Technology*, John Wiley & Sons, Inc., New York, 1956, p. 171.

[169] N. Konstantinov, *Z. anorg. Chem.*, **60**, 405 (1909); F. Weibke and G. Schrag, *Z. Elektrochem.*, **47**, 222 (1941); J. L. Haughton, *J. Iron and Steel Inst. (London)*, **115**, 417 (1927).

4-15, Fe_3P and Fe_2P have been isolated and FeP shows up, although the diagram was not extended to a high enough phosphorus content to reach this compound in pure form. As can be seen from the phase diagram, the

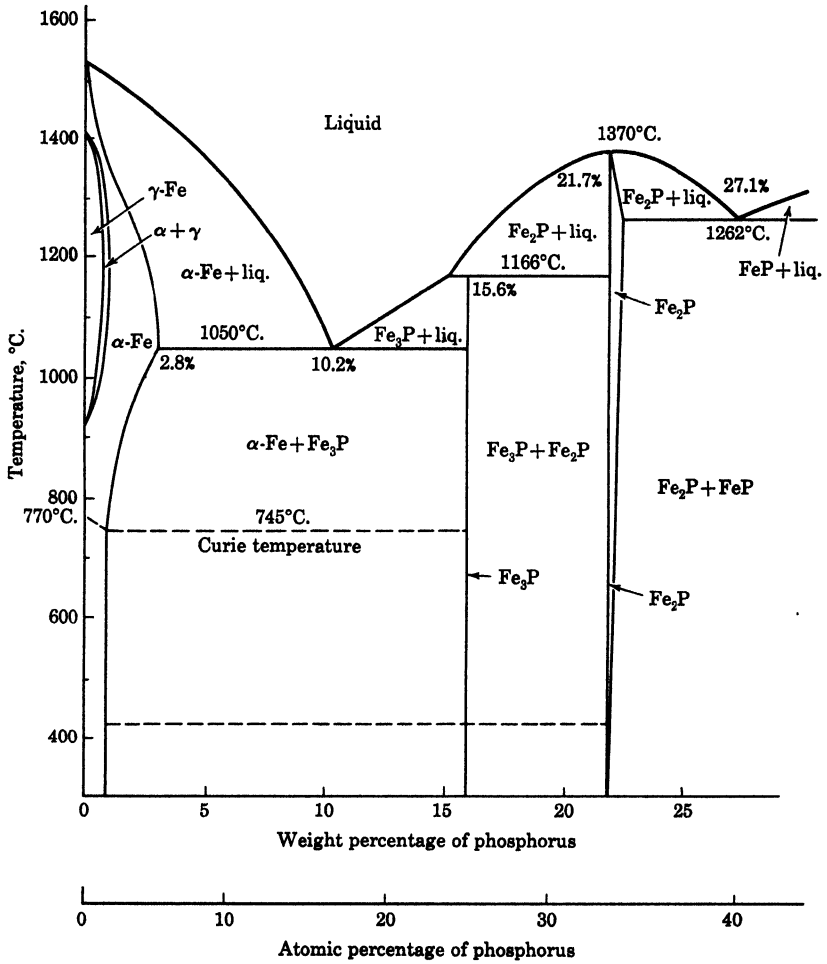


Fig. 4-15. Phase diagram of the iron-phosphorus system.

highest concentration at which phosphorus can be dissolved in solid iron corresponds to 2.8% phosphorus at 1050°C. Below this concentration of dissolved phosphorus, there is an interesting phase change from α-iron to γ-iron—a change which is affected by the amount of phosphorus dissolved

in the iron. As can be seen in Figure 4-15, the larger amounts of dissolved phosphorus (between about 0.7 and 2.8% phosphorus) prevent the formation of γ-iron. This causes the pure γ-iron to exist in a restricted region—bounded by upper and lower temperature limits of 1400 and 900°C. at 0% phosphorus and a temperature of about 1150°C. at 0.30% phosphorus. This region is called the γ-loop and is of considerable importance in steel making.[170] To the right of the γ-loop in Figure 4-15, there is a crescent-shaped region in which both α- and γ-iron are found. Calculations[170] indicate that at 1150°C., where the crescent is the widest, the $\alpha + \gamma$ region ranges from about 0.30–0.70% phosphorus.

In the phase diagram shown in Figure 4-15, it should be noted that Fe_2P at higher temperatures (around 1000°C.) exists over a small composition range as a solid solution, whereas at lower temperatures the composition of this compound is no longer variable. In the iron-phosphorus system, the solid solution corresponding to a variation in the mole fraction of phosphorus is limited, although substitution of iron by a similar metal, such as vanadium (see Figure 4-19), gives large regions of solid solution. In other words, the iron-phosphorus system exemplifies the general rule that the various metal phosphides correspond to fixed metal/phosphorus mole ratios.

In the cobalt-phosphorus phase diagram[171] which was partially completed (up to 25% phosphorus by weight), only one phosphide, Co_2P, melting at 1386°C., is shown. This phosphide shows a transition from an α- (high-temperature) to a β-form at 920°C. An eutectic occurs at 1022°C. and 16.5% phosphorus.

In the nickel-rich end of the nickel-phosphorus system,[172] three phosphides are found. These are Ni_3P, Ni_5P_2 (which occurs in an α- and a β-form), and Ni_2P. This phase diagram is shown in Figure 4-16. As was the case with Fe_2P, the β-form of Ni_5P_2 exhibits a narrow region of solid solution at the high temperatures where this form is stable.

Vapor pressure measurements have also been carried out on the phosphides of all of these metals, and a typical series of experimental curves is shown in Figure 4-17 for the compounds FeP_2 and FeP.[173] These vapor pressure curves correspond to the following equilibria:

$$4\,FeP_2(s) \longrightarrow 4\,FeP(s) + P_4(g) \qquad (4\text{-}58)$$

$$4\,FeP(s) \longrightarrow 2\,Fe_2P(s) + P_2(g) \qquad (4\text{-}59)$$

[170] H. Schrader and B. N. Bose, *Trans. Indian Inst. Metals*, **6**, 104 (1952).

[171] S. Żemczużny and J. Schepelew, *Z. anorg. Chem.*, **64**, 245 (1909).

[172] N. Kanstantinow, *Z. anorg. Chem.*, **60**, 405 (1909).

[173] W. Franke, K. Meisel, and R. Juza, *Z. anorg. u. allgem. Chem.*, **218**, 346 (1934).

The heats of the reactions shown above in equations 4-58 and 4-59 are 67.0 and 80.2 kcals., respectively. It should also be noted that the heat of formation of Fe_2P from iron and red phosphorus is -34.5 kcal. The vapor-pressure equations are given below.

For FeP_2 in the temperature range of 900–1000°C.

$$\log p_{\text{mm.}} = -14{,}650/T + 14.469 \qquad (4\text{-}60)$$

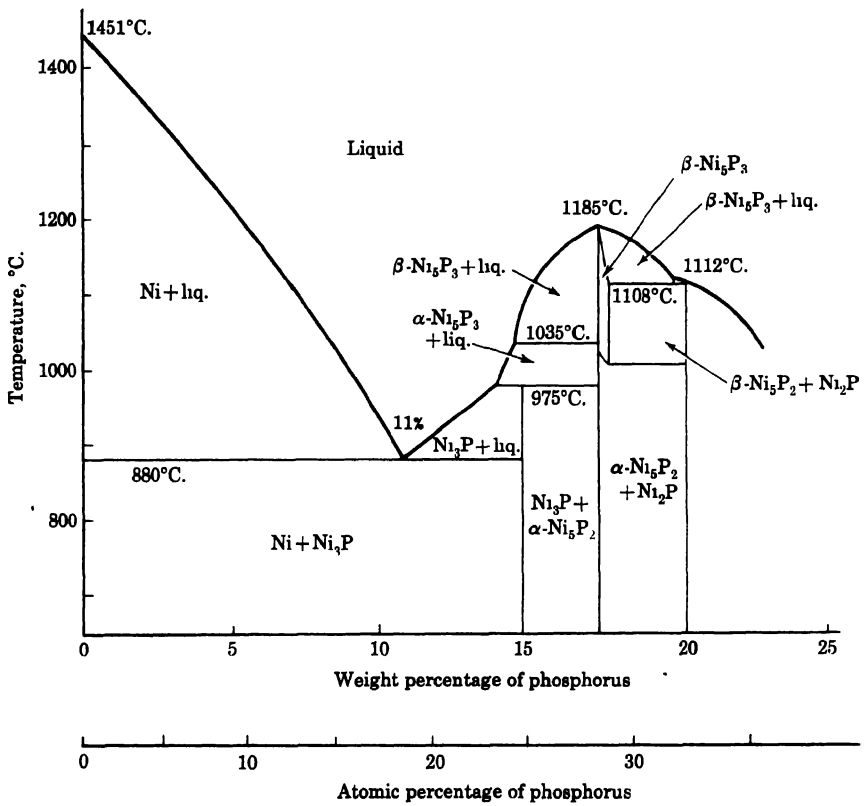


Fig. 4-16. Phase diagram of the nickel-phosphorus system.

For FeP in the temperature range of 1000–1200°C.

$$\log p_{\text{mm.}} = -17{,}540/T + 13.210 \qquad (4\text{-}61)$$

According to equation 4-60 the partial pressure of P_4 vapor reaches 1 atm. at about 990°C.

In the cobalt system, the triphosphide decomposes[174] directly to the monophosphide as shown by the following equation, which has a heat of reaction of 71.6 kcal. The partial pressure of P_4 vapor corresponding to this decomposition is also given below for the temperature range of 900–1100°C.

$$2\ CoP_3(s) \longrightarrow 2\ CoP(s) + P_4(g) \qquad (4\text{-}62)$$

$$\log p_{mm} = -15{,}650/T + 14.397 \qquad (4\text{-}63)$$

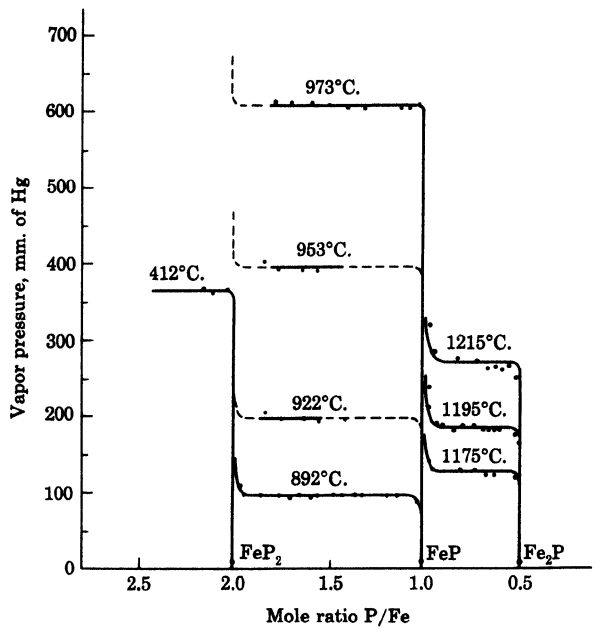


Fig. 4-17. Measured partial pressures of phosphorus over mixtures of iron and phosphorus which were fused together.

In the nickel-phosphorus system a series of stepwise thermal decompositions have been found as shown below

$$4\ NiP_3(s) \longrightarrow 4\ NiP_2(s) + P_4(g) \qquad (4\text{-}64)$$

$$24/7\ NiP_2(s) \longrightarrow 4/7\ Ni_6P_5(s) + P_4(g) \qquad (4\text{-}65)$$

$$2\ Ni_6P_5(s) \longrightarrow 6\ Ni_2P(s) + P_4(g) \qquad (4\text{-}66)$$

The heats of these reactions are 43, 57, and 63 kcals., respectively, and the temperature at which the partial pressure of P_4 vapor reaches 1 atm. is

[174] W. Biltz and M. Heimbrecht, *Z. anorg. u. allgem. Chem.*, **241**, 349 (1939).

662°C. over NiP_3 and 865°C. over Ni_6P_5. The partial pressures of P_4 vapor corresponding to the three decomposition reactions given above are:

For NiP_3

$$\log p_{mm.} = -9{,}340/T + 12.865 \tag{4-67}$$

For NiP_2

$$\log p_{mm.} = -12{,}430/T + 14.315 \tag{4-68}$$

For Ni_6P_5

$$\log p_{mm.} = -13{,}740/T + 14.951 \tag{4-69}$$

In addition to preparing these phosphides directly from the elements or by decomposing the phosphide with a higher vapor pressure to one with a lower vapor pressure, the cobalt and nickel triphosphides have been made in an interesting manner based on the properties of the tin phosphides.[116,117] In this procedure a 5% alloy of cobalt or nickel with tin is heated with excess phosphorus in a sealed container at 500°C. After cooling, SnP_3 is converted to Sn_3P_4 by heating in a vacuum at 350°C. The latter compound is soluble in hydrochloric acid, so that the more inert cobalt or nickel triphosphide is left behind. In this preparation, formation of a considerable amount of the solid, yellow hydrogen phosphide, P_2H, was noted.[117]

Phosphides of all of these metals have also been made in crystalline form by electrolysis of fused sodium phosphate melts containing the heavy metal oxide. In this way there have been prepared FeP, Fe_2P, Fe_3P, CoP, Co_2P, Ni_2P, Ni_5P_2, and Ni_3P, as well as another nickel phosphide not obtained by other techniques and having an analysis corresponding to Ni_5P_6. In Figure 4-18 a graphical representation is given of the variation of the phosphorus content of the phosphides plated onto the electrode from melts having different Fe_2O_3/P_2O_5 mole ratios. As can be seen from this chart, there is a reasonably wide range of melt compositions which give a pure phosphide. For example, to get pure FeP, the Fe_2O_3/P_2O_5 mole ratio in the bath may be varied from 1/20 to 1/8.

The cobalt phosphide, Co_3P, has not been shown to exist in pure form. In view of the fact that Fe_3P and Ni_3P decompose on melting, this is not surprising. However, small amounts of cobalt are found in schreibersite, which has the general composition $(Fe, Ni, Co)_3P$ with Fe > Ni > Co. This is probably due to stabilization of the Co_3P by the formation of a solid solution with the isomorphous Fe_3P and Ni_3P. However, pure Co_3P has been reported to be one of the products formed by the action of sodium hypo-

phosphite on cobalt salts.[175] These same authors also report the formation of Co_2P_3, Co_3P_2, Co_4P, and CoP. In view of the difficulties previously described in studying the reaction of phosphine with metal salts, as well as the instability of some intermediate products made in this way, the formation of unusual cobalt phosphides from aqueous solution using sodium hypophosphite should be viewed with skepticism. However, in spite of these comments, it should be noted that the known nickel phosphides Ni_5P_2 and

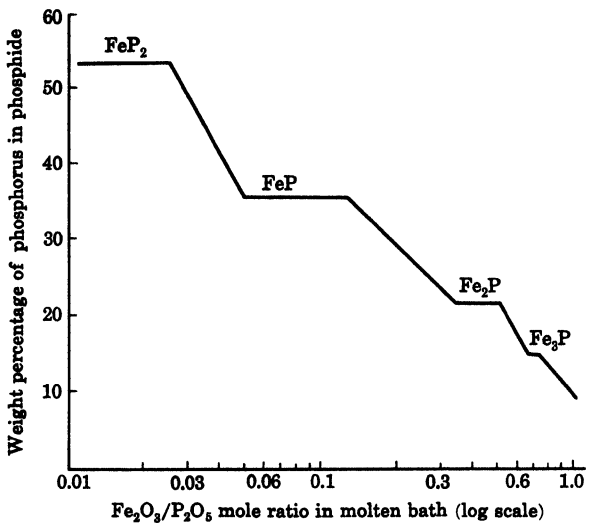


Fig. 4-18. Variation in the composition of the phosphide obtained by electrolyzing a sodium phosphate melt containing Fe_2O_3. The Fe_2O_3/P_2O_5 mole ratio in the melt is plotted against the weight per cent of phosphorus in the phosphide. All data refer to 850°C. except for the upper part of the curve corresponding to FeP_2.

Ni_2P were prepared by the action of sodium hypophosphite on nickel salts.[175] These reactions should be reinvestigated.

If the hypophosphite work is ignored, it is seen that there are more phosphides known for nickel than there are for any other metal. In addition, two of the phosphides, Ni_5P_5 and Ni_5P_2, have rather unusual formulas. Only one other accepted phosphide has the latter formula, and that is the phosphide of the related element palladium. Cu_5P_2 has been reported in the older literature,[78] but no recent investigator has found evidence for this compound. An x-ray investigation of these two nickel phosphides, as

[175] R. Scholder and H. Heckel, *Ber.*, **64B**, 2870 (1931); C. Paal and L. Friederice, *ibid.*, **64B**, 256 (1931).

well as the rhodium phosphide having the composition Rh_5P_4 would be of interest. It is possible that Ni_6P_5 and Rh_5P_4 are related to the phosphorus-deficient phases of the "monophosphides" of zirconium, niobium, and tantalum.

All of the phosphides of iron, cobalt, and nickel are grey to grey-black, with a metallic appearance. They conduct electricity, and the lower phosphides are ferromagnetic. They are all insoluble in water and dilute min-

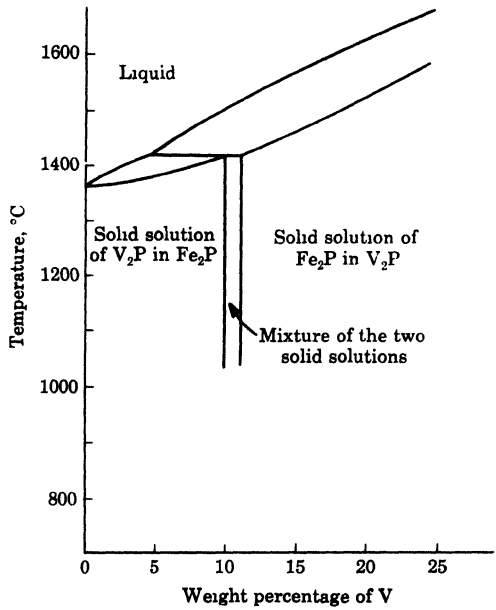


Fig. 4-19. Solid solutions in the Fe_2P-V_2P system, showing one phase identical to Fe_2P although containing vanadium and another phase which is still richer in vanadium.

eral acids but dissolve in hot nitric acid. The magnetic moment of iron in Fe_2P is 14 magnetons—the same as in the neutral atom (unionized Fe).

Structural data on Fe_2P and FeP_2 are reported in Table 4-4. In FeP_2, which has a marcasite type of structure, there are pairs of phosphorus atoms, at a distance of 2.17 A. from each other. This is the same P-P distance that is found in black phosphorus. The pairs of joined phosphorus atoms are also relatively close to each other, with the shortest P-P distance between pairs being 2.73 A. For comparison, in Fe_2P the shortest P-P distance is 3.45 A. The shortest distance between iron atoms is 2.73 A. in FeP_2 and 2.63 A. in Fe_2P. These values are 9% and 4% larger than the Fe-Fe distances in metallic iron. The structure of Fe_2P is similar to those

of the other transition metal phosphides—each iron atom has three or four nearest-neighbor phosphorus atoms, depending on the location of the iron atom; and two-thirds of the phosphorus atoms have six nearest-neighbor iron atoms, while one-third have nine nearest-neighbor iron atoms.

Phase-diagram studies have been carried out on a number of ternary systems involving iron and phosphorus. Thus, the following systems involving phosphorus, iron, and another metal have been investigated either fully or in part: Fe—Co—P,[176] Fe—Ni—P,[156,177] Fe—Cr—P,[156,178] Fe—Mn—P,[156,179] Fe—W—P,[163] Fe—Mo—P,[180] Fe—V—P, Fe—Zn—P,[181] Fe—Cu—P,[130] Fe—Sn—P,[113] Fe—Al—P,[182] and Fe—Sb—P.[183] An interesting transition between two solid solutions in the Fe—V—P system is shown in Figure 4-19. This figure again demonstrates that replacement of a given metal in a phosphide by a similar metal gives extended regions of solid solution

In addition to the systems involving phosphorus, iron, and another metal, systems based on iron, phosphorus, and a nonmetallic element other than phosphorus have also been studied, as shown by the following examples which, again, have been only partially investigated in most cases: Fe—P—C,[184,185] Fe—P—C—Si,[186] Fe—P—Si,[187] Fe—P—S,[188] Fe—P—O,[189] and

[176] J. Berak, *Hutnik*, **18**, 6 (1951); *Arch. Eisenhuttenw.*, **22**, 131 (1951).

[177] R. Vogel, *Abhandl. Ges. Wiss. Gottingen, Math.-physik. Kl.*, **3**, No. 6, 1 (1932); R. Vogel and H. Baur, *Arch. Eisenhuttenw.*, **5**, 269 (1931/32).

[178] R. Vogel and G. W. Kasten, *Arch. Eisenhüttenw.*, **12**, 387 (1939).

[179] R. Vogel and J. Berak, *Arch. Eisenhuttenw.*, **23**, 217 (1952).

[180] R. Vogel and D. Horstmann, *Arch. Eisenhüttenw.*, **24**, 369 (1953).

[181] R. Vogel and D. Horstmann, *Arch. Eisenhuttenw.*, **24**, 247 (1953)

[182] R. Vogel and H. Klose, *Arch. Eisenhüttenw.*, **23**, 287 (1952).

[183] R. Vogel and D. Horstmann, *Arch. Eisenhuttenw.*, **23**, 127 (1952).

[184] R. Vogel, *Arch. Eisenhuttenw.*, **3**, 369 (1929); E. Scheil, *Mitt. Forsch.-Insts. Ver. Stahlwerke A.-G. Dortmund*, **1**, 1 (1928), N. S. Konstantinov, *J. Russ. Phys.-Chem. Soc.*, **50**, I, 311 (1918).

[185] J. E. Stead, *J. Soc. Chem. Ind. (London)*, **33**, 173 (1914); M. Kunkele, *Mitt. Kaiser-Wilhelm-Inst Eisenforsch. Dusseldorf*, **12**, 23 (1930); Y. Yamamoto, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **9**, 838 (1930); F. Rogers, *Nature*, **114**, 275 (1924).

[186] O. von Keil and R. Mitsche, *Arch. Eisenhuttenw.*, **3**, 149 (1929); P. Bardenheuer and M. Kunkele, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Dusseldorf*, **12**, No. 3, 33 (1930); *ibid.*, **12**, No. 4, 33 (1930).

[187] W. Hummitzsch and F. Sauerwald, *Z. anorg. u. allgem. Chem.*, **194**, 113 (1930); F. Sauerwald, W. Teske, and G. Lempert, *ibid.*, **210**, 21 (1933); H. Hamemann and H. Voss, *Zentr. Huttens.- u. Walzwerke*, **31**, 245 (1927).

[188] R. Vogel and O. de Vries, *Arch. Eisenhuttenw.*, **4**, 613 (1931); also see H. Lofquist, *Tek. Tidskr, Uppl. C. Kemi och Bergvetenskap*, **67**, 33 (1937); *Chem. Zentr.*, **1937**, II, 126.

[189] H. Schackman and W. Krings, *Z. anorg. u. allgem. Chem.*, **213**, 161 (1933); F. Kanz, E. Scheil, and E. H. Schulz, *Arch. Eisenhüttenw.*, **8**, 67 (1934); W. Krings, *Z. Metallkunde*, **26**, 247 (1934).

a small amount of information on the system Fe—P—Si—O.[190] These studies were primarily directed toward a better understanding of steel making as, for example, in the Bessemer process.[191] An interesting phenomenon which has been investigated rather thoroughly is the phosphide eutectic in cast iron.[185] Molten iron containing carbon and phosphorus can congeal as either metastable mixtures of iron plus iron carbide and iron phosphide or as stable mixtures of iron plus graphite and iron phosphide. The ternary phosphide eutectic is found in the former case. In cooling a material such as cast iron, the last of the melt to solidify is the eutectic mixture between Fe, Fe_3P, and Fe_3C. On slow cooling, some of the carbon of the iron carbide diffuses out of the eutectic and forms a fringe of pearlite around the region of the eutectic mixture, but in diffusing into the surrounding solid solution of phosphorus in iron, the carbon precipitates some Fe_3P, which then appears as laminae in juxtaposition to the pearlite. In this manner, fringes consisting of iron saturated with carbon and phosphorus, iron phosphide, and iron carbide are formed.

Due to the action described above and other effects, the phosphorus content of most steels is reduced to about 0.06% or even lower. However, in low-carbon steels, phosphorus is considered as a useful alloying agent, the content of which is intentionally increased.[170] Thus, the tensile and yield strengths of a low-carbon steel are roughly doubled by the addition of 0.9% phosphorus.[192] Use of phosphorus also increases[193] the creep strength of some steels and has a favorable effect[192] on the corrosion resistance of the steel in moist atmospheres. Phosphorus also causes the formation of an adherent scale which prevents steel sheets from sticking together when rolled.

In the commercial manufacture of elemental phosphorus, the iron present in the phosphate ore forms iron phosphides which are known under the generic name of ferrophosphorus. In addition to its formation as a by-product, ferrophosphorus for metallurgical use is sometimes made commercially by reducing phosphate rock in the presence of iron.[194] Commercial ferrophosphorus usually contains about 23–26% phosphorus by weight, corresponding to an impure mixture of Fe_2P and FeP. Most of the ferro-

[190] F. Korber and W. Oelsen, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf*, **19**, No. 9, 109 (1936).

[191] H. Wentrup, *Stahl u. Eisen*, **62**, 749 (1942); *Tech. Mitt. Krupp Forschungsber.*, **5**, 141 (1942).

[192] E. d'Amico, *Ferrum*, **10**, 289 (1912–1913); C. H. Lorig and D. E. Krause, *Metals & Alloys*, **7**, 69 (1936).

[193] H. C. Cross and D. E. Krause, *Metals & Alloys*, **8**, No. 2, 53 (1937).

[194] For example, see P. Dutoit, *J. four élec.*, **47**, 16, 49 (1938).

phosphorus which is produced is employed in iron metallurgy, but there is a considerable literature on the conversion of ferrophosphorus into other products, such as the phosphates or phosphorus sulfides. Since silicon is an undesirable impurity in ferrophosphorus for use in iron metallurgy, methods have been developed for its removal.[195,196]

A typical process[197] for utilizing ferrophosphorus consists of roasting it with soda ash and salt and leaching it in several steps to produce hydroxylapatite, trisodium orthophosphate, lead chromate, and vanadium pentoxide as valuable products. Air oxidation as well as the chlorination of ferrophosphorus has been studied.[198] Oxidation, either chemically or electrically, of ferrophosphorus in concentrated aqueous acids[196,199] and bases[198,200] has also been considered as a means of converting ferrophosphorus into salable products. Fusion of ferrophosphorus with molten NaOH, Na_2CO_3, or NaCl, either alone or as mixed melts, in the presence of air gives sodium phosphates.[196,198,200] An interesting reaction between ferrophosphorus and sodium carbonate in a vacuum to give metallic sodium as one of the products has been described[201] in the patent literature. Instead of sodium salts, ferrophosphorus can be heated with calcium salts, such as limestone, to give calcium phosphates said to be suitable for fertilizers or animal-feed supplements.[196] By heating ferrophosphorus with pyrites, some of the phosphorus is recovered as phosphorus sulfides.[202] A number of other reactions of ferrophosphorus have also been investigated.[196,200]

Phosphides of the Platinum Group Metals

A number of phosphides of the Group VIII elements belonging to the second and third long periods have been reported. Those which have been observed in the course of vapor pressure and x-ray studies are listed here.

[195] B. G. Klugh, U. S. Pat. 2,476,418 (1949, assigned to Monsanto Chem. Co.).

[196] E. L. Newman and L. D. Copeland, Analytical Index of Chemical Engineering Publications, Patents, and Reports, *Tenn. Valley Author. Chem. Eng. Rept. No.* 10, Wilson Dam, Alabama, 1954, pp. 28–31.

[197] L. H. Banning, W. E. Anable, and R. T. C. Rasmussen, *J. Metals*, **5**, 423 (1953), also in *AIME Trans.*, 197, 423 (1953); L. H. Banning and W. E. Anable, U. S. Pat. 2,654,655 (1953).

[198] F. A. Henglein and F. Stoeckhert, *Beiheft Z. Ver. deut. Chem.*, No. 27, 24 pp. (1937); *Angew. Chem.*, **50**, 380 (1937).

[199] For example, O. Quadrat and V. Vcelak, *Congr. chim. ind., Compt. rend. 18me congr., Nancy, Sept.–Oct.*, **1938**, 592 (1938).

[200] Unpublished Monsanto Research Reports.

[201] L. E. Bowie, U. S. Pat. 2,484,266 (1949, assigned to Monsanto Chem. Co.).

[202] V. V. Illarionov, T. I. Sokolova, and S. I. Vol'fkovich, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1945**, 94.

	RuP_2		RuP	Ru_2P			
RhP_3	RhP_2	Rh_5P_4		Rh_2P		Rh_3P	
	PdP_2				Pd_5P_2	Pd_3P	Pd_5P
	OsP_2						
	IrP_2			Ir_2P		Ir_3P	
	PtP_2					$Pt_{20}P_7$	

Rhodium triphosphide can be obtained at 800–900°C. by heating the metal with an excess of red phosphorus in an enclosed system.[203] The diphosphides of the other metals of this series can be prepared in the same way.[204–207]

With the exception of osmium diphosphide, all of the diphosphides, as well as rhodium triphosphide, decompose on heating to form lower phosphides. In this way, the compounds RuP,[207] RhP_2, Rh_5P_4,[203] PdP_2, Pd_4P_2, Pd_3P, Pd_5P,[204] Ir_2P,[206] and $Pt_{20}P_7$[204] (near the Pt_3P composition) can be obtained. On the other hand, osmium diphosphide when heated at temperatures above 1200°C. decomposes to the metal.[127]

Although the compound Rh_5P_4 is unusual, its existence has been demonstrated through vapor pressure studies and x-ray examination.[204] The compound $Pt_{20}P_7$ has been observed in a thermal analysis investigation of the platinum phosphides, and its existence has been confirmed by x-ray examination.[205] The palladium compounds Pd_5P_2, Pd_3P, and Pd_5P were all observed as a result of thermal analysis.[204]

Except for Ir_2P, which is lavender-colored as it has been prepared, all of these compounds are either grey or black—the color being darker the higher the phosphorus content. Ir_2P is very stable, hard, and extremely inert chemically It has been used as a tip on fountain pens. All of the phosphides of this group of metals are inert toward moist air and do not dissolve in strong aqueous oxidizing agents such as aqua regia or hydrogen peroxide in basic solution. In order to decompose these compounds, it is necessary to use alkali fusions.

In this group of metal phosphides, vapor pressure data have only been obtained on rhodium triphosphide, which decomposes at extremely high temperatures. The equation for this decomposition and the partial pressure computed in terms of P_4 vapor are given by the following equations.

[203] F. Faller, E. F. Strotzer, and W. Blitz, *Z. anorg. u. allgem. Chem.*, **244**, 317 (1940).

[204] G. Wiehage, F. Weibke, and W. Blitz, *Z. anorg. u. allgem. Chem.*, **228**, 357 (1936).

[205] W. Blitz, F. Weibke, E. May, and K. Meisel, *Z. anorg. u. allgem. Chem.*, **223**, 129 (1935).

[206] K. H. Söffge, M. Heimbricht, and W. Biltz, *Z. anorg. u. allgem. Chem.*, **243**, 297 (1940).

[207] W. Biltz, H. J. Ehrhorn, and K. Meisel, *Z. anorg. u. allgem. Chem.*, **240**, 117 (1939)

The vapor pressure data apply to the temperature range of 900–1000°C., at which temperatures a correction must be made for the decomposition of P_4 vapor into P_2 vapor.

$$4\ RhP_3(s) \longrightarrow 4\ RhP_2 + P_4(g) \qquad (4\text{-}70)$$

$$\log p_{mm.} = -\ 12{,}850/T + 11.713 \qquad \Delta H = 60\ \text{kcal.} \qquad (4\text{-}71)$$

Like FeP_2, the compound PtP_2 has pairs of phosphorus atoms in its structure. However, PtP_2 exhibits a pyrite-type of crystal structure. X-ray data[147] on Rh_2P and Ir_2P are given in Table 4-4. In both of these structures the phosphorus atoms are coordinated by eight metal atoms which, in turn, are surrounded by four nearest-neighbor phosphorus atoms. The Ir-Ir distance of closest approach is 2.77 A. in Ir_2P as compared to 2.71 A. in metallic iridium.

Embrittlement[208] of the platinum-group metals is caused by small amounts of phosphorus. This is due to the formation at the boundary between platinum grains of the low-melting eutectic (m.p. 588°C.) between platinum and Pt_7P_{20}. Certain alloys of platinum are more resistant to corrosion by elemental phosphorus than pure platinum. Platinum containing 1% gold, as well as an alloy of 96% Pt, 3.5% Ru, and 0.5% Nb, has been found[209] successful for use as corrosion-resistant containers for materials from which small amounts of phosphorus are generated at high temperatures.

[208] A. Jedele, *Z. Metallkunde*, **27**, 271 (1935), H. J. Frost, *Chem.-Ztg.*, **65**, 14 (1941).

[209] K. W. Krohlich, *Chem Fabrik*, **1940**, 431; J. S. Streicher, U. S. Pat. 2,384,502 (1945, assigned to the American Platinum Works).

CHAPTER 5

Hydrides, Halides, and Pseudohalides of Phosphorus and Their Organic Derivatives

HISTORY

Unlike elemental phosphorus and some of the metal phosphides which were found in alchemical days, the hydrides and halides of phosphorus have been discovered and investigated since the advent of chemistry as we know it now. Phosphine was first prepared in 1783 by Gengembre and independently in 1786 by Kirwan.[1] Discovery of the phosphorus halides, PCl_3, PCl_5, and probably PF_3, was made in France by Gay Lussac and Thénard, in England by Davy.[2] Nearly all of the other phosphorus hydrides and halides which are known today were prepared and at least partially characterized before the beginning of the 20th century.

THE PH MOLECULE

Spectra taken on mixtures of phosphorus vapor and hydrogen show the existence of a molecule, PH, which does not exist at room temperature. This molecule exhibits a prominent spectral band at 3400 A., which corresponds to the $^3\Pi \rightarrow {}^3\Sigma$ transition.[3] The ground state of this molecule is $^3\Sigma^-$. The distribution of molecular energies in the ground state has been calculated and shown to correspond to a fictive temperature of 423°C.[4]

Since a great deal of emphasis has been placed on structural regularities

[1] P. Gengembre, *Mém. Acad.*, **10**, 651 (1785); R. Kirwan, *Phil. Trans.*, **76**, 11 (1786).

[2] J. L. Gay Lussac and L. J. Thénard, *Bull. Soc. Philomath.*, **1**, 302 (1808); *J. Mines*, **25**, 70 (1809); *Ann. Chim. Phys.*, **69**, No. 1, 204 (1809); H. Davy, *Phil. Trans.*, **98**, 43 (1808); also see *ibid.*, **100**, 231 (1810); *ibid.*, **101**, 1 (1811).

[3] M. Ishaq and R. W. B. Pearse, *Proc. Roy. Soc. (London)*, **A173**, 265 (1939); *ibid.*, **A156**, 221 (1936); *Nature*, **137**, 457 (1936). R. W. B. Pearse, *Proc. Roy. Soc. (London)*, **A129**, 328 (1930); A. Budó, *Z. Physik*, **98**, 437 (1936); *Math. u. naturw. Anz. ungar. Akad. Wiss.*, **54**, 387 (1936).

[4] P. Nolan and F. A. Jenkins, *Phys. Rev.*, **50**, 943 (1936); *ibid.*, **45**, 327 (1934).

in diatomic molecules, and especially in the diatomic hydrides, the relationships of the PH molecule to all of the other diatomic hydrides have received some discussion.[5] From these correlations, the estimated value for the fundamental stretching frequency is $\omega_e = 2380$ cm.$^{-1}$, and the force constant is 3.25×10^5 dynes/cm. The P-H distance in this molecule has been found to be 1.43 A., which corresponds to a single bond. This means that this molecule has the following electronic structure.

$$\dot{\underset{\cdot\cdot}{P}}:H \qquad (5\text{-}1)$$

PHOSPHINE

Preparation of Phosphine

Phosphine, PH_3, can be made in a number of ways, the most important of which are (1) reaction of metallic phosphides with water, (2) reaction of phosphonium halides with water or alkalies, (3) hydrolysis of elemental phosphorus, and (4) thermal decomposition of the lower oxyacids of phosphorus. Elemental phosphorus and hydrogen at normal temperatures and pressures do not combine to form phosphine.[6] Although there is an equilibrium between phosphine and its constituent elements and this equilibrium has been carefully studied,[7] it is not presently practicable to make phosphine by direct combination of the elements.

The most common preparative method for phosphine involves treatment of alkali or alkaline earth metal phosphides or other highly reactive phosphides with water. Calcium phosphide is often used, and rapid techniques for preparing a calcium phosphide suitable for this purpose have been described. For example, hydroxylapatite and aluminum can be heated in a crucible to give a mixture of Ca_3P_2 and Al_2O_3.[8] When this is treated with water, phosphine is readily formed which contains small quantities of hydrogen as the major impurity. A simple preparation of aluminum phosphide has been described recently,[9] and this material is also recommended for the preparation of phosphine.

[5] For example, see R. K. Sheline, *J. Chem. Phys.*, **18**, 927 (1950); J. R. Platt, *ibid.*, **18**, 932 (1950); C. H. Douglas Clarke, *Proc. Leeds Phil. Lit. Soc., Sci., Sect.*, **5**, Pt. IV, 318 (1950).

[6] R. Dolique, *Bull. soc. chim.*, **53**, 603 (1933).

[7] V. N. Ipatiev and A. V. Frost, *Ber.*, **63B**, 1104 (1930); also see D. H. Drummond, *J. Am. Chem. Soc.*, **49**, 1901 (1927).

[8] C. Matignon and R. Trannoy, *Compt. rend.*, **148**, 167 (1909); *Bull. soc. chim.*, **6**, 266 (1909).

[9] W. E. White and A. H. Bushey, *Inorganic Syntheses*, ed. by J. C. Bailar, McGraw-Hill Book Co., New York, 1953, Vol. IV, Chapt. 3A, pp. 23–5.

Phosphine made from the various metal phosphides often contains hydrogen, diphosphine, and higher phosphorus hydrides as impurities. These can be removed by a number of techniques which have been described in the literature and are to be found in many of the references concerning phosphine given in this chapter. The very early workers often differentiated between phosphine which was and which was not spontaneously flammable. However, it has been rather carefully demonstrated[10] that the spontaneous flammability is due to the presence of diphosphine and perhaps, in some special cases, phosphorus vapor in the PH_3.

It is generally said that the purest phosphine is derived from the alkaline hydrolysis of phosphonium iodide. Phosphonium iodide is made from white phosphorus, iodine, and water, and a reliable synthesis of this material has been described.[11] Formation of phosphine through hydrolysis of elemental phosphorus and thermal decomposition of the lower oxyacids of phosphorus is described in Chapter 7.

Structure of Phosphine

Although a preliminary x-ray study has been carried out on crystalline phosphine,[12] knowledge of the structure of the PH_3 molecule comes from spectrographic data. From careful analysis of the infrared[13] and microwave[14] spectra, it is known that all three hydrogens are equivalent, with a P-H distance of 1.419 A. and an H—P—H angle of 93.7°. The work by Sirvetz and Weston on PH_2D and PHD_2 is especially accurate. For

[10] U. J. J. Leverrier, *Ann. chim. et phys.*, **60**, No. 2, 174 (1835); *ibid.*, **65**, No. 2, 257 (1837); P Thénard, *ibid.*, **14**, No. 3, 5 (1845); *Compt. rend.*, **18**, 652 (1844); *ibid.*, **19**, 313 (1844); *ibid.*, **21**, 144 (1845), *J. pharm. chim.*, **6**, No. 3, 174 (1844); *ibid.*, **8**, No. 3, 36 (1845); J. W. Retgers, *Z. anorg. Chem.*, **7**, 265 (1894); D. Amato, *Gazz. chim. ital.*, **14**, 58 (1884).

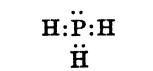
[11] J. B. Work, *Inorganic Syntheses*, ed. by W. C. Fernelius, McGraw-Hill Book Co., New York, 1946, Vol. II, Chapt. 5, pp. 141–44.

[12] G. Natta and E. Casazza, *Gazz. chim. ital.*, **60**, 851 (1930). At −170°C. PH_3 crystallizes in the cubic system. The phosphorus atoms are arranged in a face-centered structure with respect to each other, and the unit cell contains four molecules and has a dimension of 6.31 ± 0.01 A. The density is 0.896.

[13] H. H. Nielsen, *J. Chem. Phys.*, **20**, 759 (1952); V. M. McConaghie and H. H. Nielsen, *Proc. Natl. Acad. Sci. U. S.*, **34**, 455 (1948). Also see R. E. Weston, Jr., and M. H. Sirvetz, *J. Chem. Phys.*, **20**, 1820 (1952); H. H. Nielsen, *Discussions Faraday Soc.*, **1950**, No. 9, 85; R. E. Stroup, R. A. Oetjen, and E. E. Bell, *J. Opt. Soc. Amer.*, **43**, 1096 (1953); R. E. Stroup and R. A. Oetjen, *J. Chem. Phys.*, **21**, 2092 (1953); J. B. Howard, *ibid.*, **3**, 207 (1935); L. W. Fung and E. F. Barker, *Phys. Rev.*, **45**, 238 (1934); N. Wright and H. M. Randall, *Phys. Rev.*, **44**, 391 (1933).

[14] M. H. Sirvetz and R. E. Weston, Jr., *J. Chem. Phys.*, **21**, 898 (1953); C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.*, **81**, 798 (1951).

example, in PH_2D the P-H equilibrium distance is shown to be 1.4177 A. with an equilibrium bond angle of 93° 22′. Theoretical investigation[15] of the bonding in the PH_3 molecule indicates that to a great extent the P—H bonds involve *p*-orbitals, whereas, in the unshared pair of electrons, *s*-character predominates. The PH_3 molecule thus has the following electronic structure:



(5-2)

These results stem from exhaustive studies which have been made on the infrared,[13] visible,[16] and Raman[17] spectra. From the infrared work, it is shown that the principal moment of inertia of the molecule equals 6.22×10^{-40} g.-cm.^{2}. According to the selection rules, a four-atom molecule of C_{3v} symmetry, such as phosphine, will have four fundamental frequencies—two of species A (parallel and polarized) and two of species E (perpendicular, depolarized, and doubly degenerate). From the infrared data, the four fundamental frequencies are $\omega_1 = 2322.9$, $\omega_2 = 990$, ω_3 is estimated at 2328, and $\omega_4 = 1121$. These data, combined with information[7] on the equilibrium between phosphine and its constituent elements, have been used to calculate[18] the thermodynamic functions of phosphine gas.

The phosphorus nuclear magnetic resonance spectrum of phosphine shows four peaks of 1:3:3:1 relative intensity.[19] This splitting into a quadruplet is due to indirect spin-spin coupling of the phosphorus with the three hydrogen atoms. It shows that the hydrogens are covalently bonded to the phosphorus and are equivalent. The indirect spin-spin coupling also produces a 1:1 doublet in the hydrogen spectrum.

[15] A. D. Walsh, *J. Chem. Soc.*, **1953**, 2296; R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935); also see refs. 13 and 14.

[16] G. H. Cheesman and H. J. Emeléus, *J. Chem. Soc.*, **1932**, 2847; H. W. Melville, *Proc. Roy. Soc. (London)*, **A139**, 541 (1933); R. de Mallemann and P. Gabiano, *Compt. rend.*, **199**, 600 (1934) (Verdet's constant).

[17] D. M. Yost and T. F. Anderson, *J. Chem. Phys.*, **2**, 624 (1934); J. M. Delfosse *Bull. sci. acad. roy. Belg.*, **20**, 1157 (1934); M. de Hemptinne and J. M. Delfosse, *ibid.*, **21**, 793 (1935). H. Siebert, *Z. anorg. u. allgem. Chem.*, **274**, 24 (1953).

[18] D. P. Stevenson and D. M. Yost, *J. Chem. Phys.*, **9**, 403 (1941). Also see ref. 43 for correction of some errors and listing of more acceptable thermodynamic data.

[19] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

Physical Properties of Phosphine

The density and compressibility of phosphine have been carefully studied as a means of determining the atomic weight of phosphorus.[20] From these data, Ritchie found the molecular weight of PH_3 to be 34.000. which leads to an atomic weight of phosphorus of 30.977. This should be compared with the 1952 chemical atomic weight of 30.975, which is based on mass spectrograph and nuclear reaction data (see Chapter 1). These accurate determinations of density and compressibility mean that the gas imperfections of phosphine are well characterized, and that the equation of state of phosphine vapor is known with considerable precision.[21] Viscosity measurements have also been carried out on gaseous phosphine,[22] and dielectric constants[14,23] of phosphine and the deuterated phosphines are known. Large-angle scattering of electrons has been investigated in phosphine,[24] and the relative intensities of ions in a mass spectrograph have been obtained for phosphine.[25]

Liquid phosphine boils at −87.78°C. and freezes at −133.81°C. (the triple point) under its own vapor pressure of 27.33 mm. of Hg. The heat of fusion[26] is 0.270 kcal./mole, and the heat of vaporization[27] is 3.493 kcal./mole. The vapor pressure[26] of liquid phosphine is represented by the following equation.

$$\log p_{\text{cm.}} = 9.73075 - 1.7853 \times 10^{-2}T + 2.9135 \times 10^{-5}T^2 - 1.0273 \times 10^{3}T^{-1} \quad (5\text{-}3)$$

The physical constants of liquid phosphine indicate that there may be some association in the liquid,[28,29] but that this association is probably small as

[20] M. Ritchie, *Proc. Roy. Soc.* (*London*), **A128**, 551 (1930); *Nature*, **123**, 838 (1929); G. Ter Gazarian, *J. chim. phys.*, **9**, 101 (1911); J. J. van Laar, *ibid.*, **17**, 266 (1919).

[21] C. F. Curtiss and J. O. Hirschfelder, *J. Chem. Phys.*, **10**, 491 (1942); E. A. Long and E. A. Gulbransen, *J. Am. Chem. Soc.*, **58**, 203 (1936).

[22] A. O. Rankine and C. J. Smith, *Phil. Mag.*, **42**, 601 (1921).

[23] H. E. Watson, *Proc. Roy. Soc.* (*London*), **A117**, 43 (1927).

[24] C. B. O. Mohr and F. H. Nicoll, *Proc. Roy. Soc.* (*London*), **A138**, 469 (1932).

[25] H. Neuert and H. Clasen, *Z. Naturforsch.*, **7a**, 410 (1952).

[26] C. C. Stephenson and W. F. Giauque, *J. Chem. Phys.*, **5**, 149 (1937); also see K. Clusius, *Z. Elektrochem.*, **39**, 598 (1933); K. Clusius and A. Frank, *Z. physik. Chem.*, **B34**, 405 (1936); K. Clusius and K. Weigand, *ibid.*, **B46**, 1 (1940).

[27] A. Frank and K. Clusius, *Z. physik. Chem.*, **B42**, 395 (1939); L. A. K. Staveley and W. I. Tupman, *J. Chem. Soc.*, **1950**, 3597.

[28] A. A. Durrant, T. G. Pearson, and P. L. Robinson, *J. Chem. Soc.*, **1934**, 730. Some of these values are obsolete and should be checked with ref. 29 and with ref. 43.

[29] D. M. Yost and H. Russell, *Systematic Inorganic Chemistry*, Prentice-Hall Inc., New York, 1946, Chapt. 7.

TABLE 5-1
Some Physical Properties of Phosphorus Hydrides, Halides, and Halogenides

No	Formula	Appearance at room temperature and normal pressures	Boiling point (°C.)	Heat of vaporization (kcal.)	Trouton's constant[a]	Density of liquid (g./cc)
1.	PH_3	Colorless gas	−87 8	3 49	18 8	
2	P_2H_4	Colorless liquid	+56	6 89	21	
3	PF_3	Colorless gas	−101 8	2 95	23 1	
4	PF_2Cl	Colorless gas	−47 3	4 20	19 1	
5	$PFCl_2$	Colorless gas	+13 85	5 95	20 7	
6	PCl_3	Colorless liquid	+76	7 28	21 7	1 575 (21°)
7.	PF_2Br	Colorless liquid	−16 1	5 72	22 3	
8.	$PFBr_2$	Colorless liquid (tan when impure)	+78 4	7 62	21 7	2 181 (0°)
9	PBr_3	Colorless liquid (tan when impure)	+172 8	9 79		2 852 (15°)
10.	PI_3	Deep red, hexagonal crystals, deliq	>200 (decomp)			
11.	P_2Cl_4	Colorless, oily liquid	ca +180			
12.	P_2I_4	Pale orange, triclinic crystals	Decomp			
13.	PF_5	Colorless gas	−84 5	4 11	21 8	
14	PF_3Cl_2	Colorless gas	+10			
15.	PCl_5	Greenish white, tetragonal crystals	+160 (subl)	15 5		1 60 (solid at 160°)
16	PF_3Br_2	Solid	ca 106			
17	PBr_5	Reddish yellow, rhombohedral crystals	106 (decomp)	13 0 (subl.)		
18.	POF_3	Colorless gas	−39 7	5 55	23 8	
19	POF_2Cl	Colorless gas	+3 1	6 08	22 0	1 656 (0°)
20.	$POFCl_2$	Colorless liquid	+52 9	7 40	22 7	1 593 (0°)
21.	$POCl_3$	Colorless liquid	+105 8	8 06	21 3	1 712 (0°)
22	POF_2Br	Colorless liquid	+31 6		23 4	
23	$POFBr_2$	Colorless liquid	+110 1		19 6	
24.	$POBr_3$	Colorless liquid (tan when impure)	+191 7	9 08		
25.	PSF_3	Colorless gas	−52 2	4 68	21 1	
26.	PSF_2Cl	Colorless gas	+6 3	5 70	20 4	
27.	$PSFCl_2$	Colorless liquid	+64 7	6 89	20 3	
28	$PSCl_3$	Colorless liquid	+125			
29	PSF_2Br		+35 5			
30.	$PSFBr_2$		+125 3			
31	$PSBr_3$	Yellow cubic crystals	+212 (decomp)			
32	$PCl_2(NCS)$	Colorless liquid	+148	12 6	29 9	1 54 (25°)
33.	$PCl(NCO)_2$	Colorless liquid	+134 6	11 2	27 4	1 50 (25°)
34.	$P(NCO)_3$	Colorless liquid	+169 3	11 9	26 8	1 439 (25°)
35.	$PO(NCO)_3$	Colorless liquid	+193 1	13 41	28 8	1 570 (25°)
36.	$PO(NCS)_3$	Colorless liquid	+300 1	14 82	25 8	1.484 (25°)
37.	$PS(NCO)_3$	Colorless liquid	+215	ca. 16	ca. 33	1.538 (25°)

[a] Trouton's constant = heat of vaporization at boiling point/boiling point in °K. For heat of vap. in calories and b.p. in °K., Trouton's constant for nonassociated liquids of a molecular weight around 100 and not too high a boiling point is about 21. Associated liquids give higher values Trouton's constant for water is 26.0, for ammonia is 23.6.

[b] $\log p_{mm.} = -A/T + B$.

[c] Based on α-white phosphorus as standard

TABLE 5-1 (*continued*)

No	Constants in the vapor pressure equation[b] A_{liq}	B_{liq}	A_{solid}	B_{solid}	Melting point (°C.)	Heat of fusion (kcal.)	Critical temperature (°C.)	Critical pressure (atm.)	Heat of formation[c] (kcal.)	Refs.
1.	See eq. 5-3 in text		895 700	7 86434	−133 8	0 27	+51	64	+2 29	43
2.	1498	7 330			−99					101
3.	861 9	7 9269			−151 5		−2 05	42 69	−189(g)	D,43
4	939 7	7 043			−164 8		89 17	44 61		43,121
5	1308	7 439			−144 0		189 84	49 3		43,121
6.	1657 3	7 6455			−93 6		285 5		−74 4(l)	A,B,C,43
7.	1217 9	7 620			−133 8		113			43,123
8.	1667	7 6248			−115 0		254			43,123
9	2137 9	7 67865			−40 5				−46 5(l)	A,C,43
10					+61 2				−10 9(s)	43
11					−28					43,171
12					+124 5				−19 76(s)	43,174
13	898 9	7 646	1518 8	11 101	−93 7	2 84				E,43
14					−8					180
15			6724 22	19 1978	+167		372		−106 5(s)	F,43
16.					−20					180
17.					<100 (decomp.)				−60 6(s)	43
18	1207	8 0524	1984 7	11 3755	−39 1	3 60	73 3	41 8	−260(g)	D,43
19	1328 3	7 6904			−96 4		150 6	43 4		43,225
20	1618 23	7 8440			−80 1					43,225
21					+1 1	3 11			−144 1(l)	B,C,G,43
22	1550 0	7 9662			−84 8					43
23	1642 9	7 1687			−117 2					43
24					+55				−110 1(s)	H,43
25					−148 8		72 8	37 7		43
26					−155 2		166	40 9		260
27.					−96 0					260
28.					−35					43
29.					−136 9					260
30.					−75 2					260
31.	2641 9	8 3383	3196 2	10 105	+37 8					I
32.	2756 6	9 42681			−76					269,267
33.	2445 2	8 87981			−50					269,267
34	2595	8 7455			−2					267,268
35.	2931	9 1682			+5 0					267,268
36	3240	8 5330			+13 8					267,268
37.	3492	10 032			+8 8					267,268

A. K Arii and M. Kawabata, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **17**, 299 (1938), M. van Driel and H Gerding, *Rec. trav. chim.*, **60**, 943 (1941).

B. E Neale and L. T. D. Williams, *J. Chem. Soc.*, **1954**, 2156; *ibid.*, **1952**, 4535.

C T. Charnley and H. A. Skinner, *J. Chem. Soc.*, **1953**, 450.

D G. Tarbutton, E. P. Egan, Jr., and S. G. Frary, *J. Am. Chem. Soc.*, **63**, 1782 (1941).

E. R. Linke and W. Rohrmann, *Z. physik. Chem.*, *B35*, 256 (1937).

F. E. B R. Prideaux, *Trans. Faraday Soc.*, **6**, 155 (1911).

G. G. P. Luchinskii and A. I. Likhacheva, *J. Phys. Chem.* (*U.S.S.R.*), **9**, 65 (1937), K. Arii, *Science Repts Tohoku Imp. Univ., First Ser.*, **22**, 182 (1933), *Bull. Inst. Phys. Chem Research (Tokyo)*, **8**, 545 (1929).

H. M van Driel, *Rec. trav. chim.*, **61**, 718 (1942)

I I. Nitta and S Seki, *J Chem Soc Japan*, **62**, 581 (1941)

compared to water or even liquid ammonia. When compared with the hydrides of neighboring elements in the periodic table,[30] it is seen that phosphine shows little or no evidence of hydrogen bonding.

The surface tension[28,31] of liquid phosphine has been measured as a function of temperature. At −100°C. it is 22.0 dynes/cm. The density[32] of liquid phosphine is given by the following relation in which t stands for the temperature in °C.

$$d = 1.76705 - 0.0009222\ (t - 20)^{\circ} \tag{5-4}$$

The critical constants[33,34] for phosphine are 51°C. and 64 atm.

In the solid state, four modifications of phosphine are known,[26] with transitions at −185.06°C., −223.73°C., and −242.87°C. Since the transition at −223.73°C. is extremely sluggish on cooling (with several days being needed to effect transformation to the lower temperature form), the form which is stable between −185.06 and −223.73°C. can be readily obtained at lower temperatures where it is unstable. In a small temperature range around absolute zero, this supercooled form exhibits an abnormally high heat capacity. The high-temperature form, stable above −185.0°C., has a cubic crystal structure.[13] Its sublimation pressure is given by the following equation[26] for temperatures above −145°C.

$$\log p_{\text{cm.}} = -895.700/T + 6.86434 \tag{5-5}$$

The lower temperature studies on the supercooled and stable modifications of phosphine have made possible a test of the Third Law of Thermodynamics. In one form this law states that at absolute zero, the entropies of all polymorphic modifications of a pure substance are equal. This was found to be the case for the supercooled and lowest temperature modifications of phosphine, which offers one of the few clear-cut tests of the Third Law.[26]

The solubility of phosphine in water is relatively low,[35] as is shown in Figure 5-1, where the solubility is reported in terms of the Ostwald solubility coefficient (β = conc. of solute in solution phase/conc. of solute in the gas phase). The solubility coefficient is independent of pressure from 100

[30] R. W. Taft and H. H. Sisler, *J. Chem. Educ.*, **24**, 175 (1947).

[31] B. D. Steele and D. McIntosh, *Z. phys. Chem.*, **55**, 140 (1906).

[32] S. Dobinski, *Z. Physik*, **83**, 129 (1933).

[33] P. A. Guye, *Mem. Sci. Geneve*, **35**, 547 (1909); E. Briner, *J. chim. phys.*, **4**, 476 (1906); A. Leduc and P. Sacerdote, *Compt. rend.*, **125**, 397 (1897).

[34] S. Skinner, *Proc. Roy. Soc. (London)*, **42**, 283 (1887); L. Cailletet and L. Bordet *Compt. rend.*, **95**, 58 (1882).

[35] R. E. Weston, *J. Am. Chem. Soc.*, **76**, 1027 (1954).

to 700 mm. so that Henry's law is obeyed, at least below 1 atm. Since dissolved neutral salts have the same general effect on the solubility of phosphine in water as do acids and bases, it can be concluded that phosphine solutions in water are, for all practical purposes, neither acidic nor basic. This is born out by pH measurements. Phosphine dissolved in water undergoes a gradual decomposition into phosphorus, hydrogen, and the solid phosphorus hydride of the approximate formula P_2H. A solid hydrate

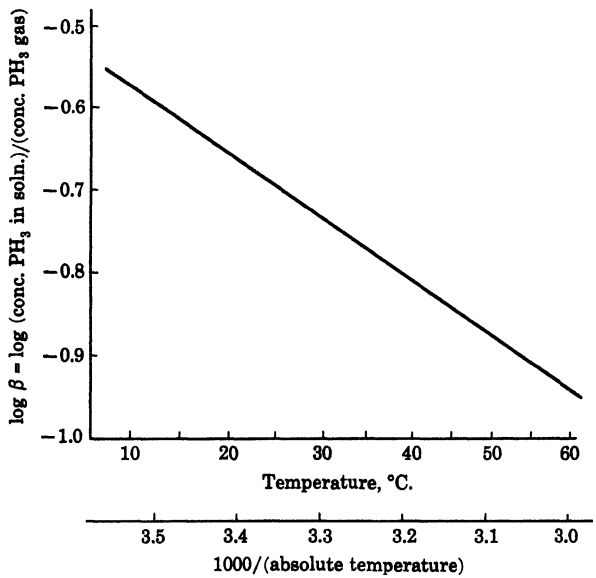


Fig. 5-1. Solubility of phosphine in water, where β is the Ostwald solubility coefficient.

of phosphine has been reported.[34] Although no analyses of this crystalline hydrate have been given, it has been assumed in the early literature to have the formula, $PH_3 \cdot H_2O$ or PH_4OH. However, a recent theoretical consideration[36] concerning the hydrates of gases chemically inert to water indicates that the formula of hydrated phosphine crystals should be $PH_3 \cdot 5.9H_2O$. The water in such a crystal would be packed into the voids between the PH_3 molecules.

Although no direct measurement of the acid-base strength of phosphine has been reported, the acidic and basic dissociation constants of phosphine

[36] W. F. Claussen, *J. Chem. Phys.*, **19**, 1425 (1951).

have been estimated from kinetic data on the exchange of hydrogen between water and phosphine.[37] These dissociation constants are

$$K_{acid} = \frac{[PH_2^-][H_2O^+]}{[PH_3][H_2O]} \backsimeq 1.6 \times 10^{-28} \quad \text{at } 27°C. \tag{5-6}$$

$$K_{base} = \frac{[PH_4^+][OH^-]}{[PH_3][H_2O]} \backsimeq 4 \times 10^{-28} \quad \text{at } 27°C. \tag{5-7}$$

In liquid ammonia, phosphine acts as a conductor.[38] On electrolysis of a solution of phosphine in liquid ammonia, elemental phosphorus is deposited on the anode. Apparently a salt-like compound is formed between ammonia and phosphine, perhaps $NH_4^+(PH_2^-)$. Phosphine is considerably more soluble in cyclohexanol than in water. It has been found[39] that 286 ml. of phosphine dissolve in 100 ml. of cyclohexanol at 25°C. and 766 mm. of Hg.

From theoretical grounds, it was concluded that substituted phosphines having three different ligands attached to the phosphorus would be optically active and resolvable.[40] However, because of chemical difficulties this has not as yet been done.[41]

Reactions of Phosphine

Exchange of hydrogen between gaseous phosphine and liquid water,[37] as well as the mercury-photosensitized exchange between phosphine and molecular hydrogen,[42] both in the gas phase, has been investigated. The activation energy, in the first case, was found to be 17.6 kcal./mole and, in the second case, 15.0 kcal./mole.

The dissociation of phosphine has been carefully studied,[7] and the exper mental data have been compared with the other thermodynamic data available on phosphine.[43] The equilibrium constant, $K_{atm.}$, is given in Figure 5-2 as a function of temperature. According to these constants, phosphine should be strongly dissociated even at room temperature. How-

[37] R. E. Weston and J. Bigeleisen, *J. Am. Chem. Soc.*, **76**, 3074 (1954); *J. Chem. Phys.*, **20**, 1400 (1952).

[38] P. Royen, *Z. anorg. u. allgem. Chem.*, **235**, 324 (1938).

[39] G. Cauquil, *J. chim. phys.*, **24**, 53 (1927).

[40] J. F. Kincaid and F. C. Henriques, Jr., *J. Am. Chem. Soc.*, **62**, 1474 (1940).

[41] For some comments on this matter by an expert in the resolution of optically active phosphorus compounds see F. G. Mann, *J. Chem. Soc.*, **1945**, 65.

[42] H. W. Melville and J. L. Bolland, *Proc. Roy. Soc.* (*London*), **A160**, 384 (1937).

[43] T. D. Farr, Phosphorus, "Properties of the Element and Some of Its Compounds," *Chem. Eng. Rept. No.* 8, Tennessee Valley Authority, Wilson Dam, Ala., 1950.

ever, the rate of attainment of the dissociation is immeasurably slow at temperatures below several hundred degrees Centigrade; and, at room temperature or below, phosphine is essentially completely stable with respect to dissociation:

$$4\ PH_3(g) \longrightarrow P_4(g) + 6\ H_2(g),\quad \Delta H_0^0 = 1.53\ \text{kcal.} \tag{5-8}$$

$$K_{\text{atm.}} = \frac{p_{P_4}(p_{H_2})^6}{(p_{PH_3})^4} = \frac{x_{P_4}x_{H_2}^{\ 6}}{x_{PH_3}^{\ 4}} \times p_{\text{total}}^{\ 3} \tag{5-9}$$

where x = the mole fraction; $x_{P_4} + x_{H_2} + x_{PH_3} = 1$.

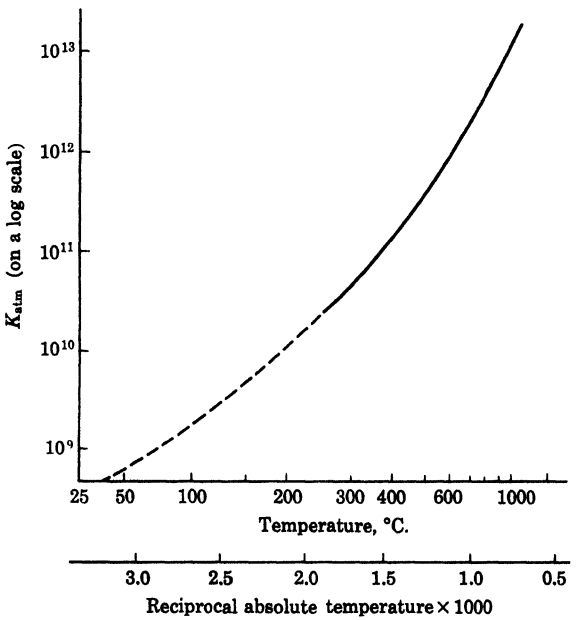


Fig 5-2. Dissociation equilibrium for phosphine. $K_{atm} = (p_{P_4})(p_{H_2})^6/(p_{PH_3})$.[4]

The rate of decomposition of phosphine has been the subject of several studies.[44] The thermal decomposition is a first-order reaction, exhibiting a rate constant for loss of PH_3 of about 8×10^{-3} sec^{-1} at 500°C. Under most experimental conditions, the phosphorus is deposited as the red modification.

[44] H. W. Melville and H. L. Roxburgh, *J. Chem. Soc.*, **1933**, 586; M. Trautz and D. S. Bhandarkar, *Z. anorg. u. allgem. Chem.*, **106**, 95 (1919); H. W. Melville, *Nature*, **129**, 546 also see p. 247 of ref. 29.

The reaction of phosphine with oxygen has been extensively studied and shown to be a branching chain reaction,[45] similar in many respects to the oxidation of white phosphorus discussed in Chapter 4. As shown in Figure 5-3, there are upper and lower critical pressures in the oxidation of phosphine as are found in the oxidation of phosphorus vapor (compare with Fig. 4-3). The equation for the lower limit of the explosion region in the oxida-

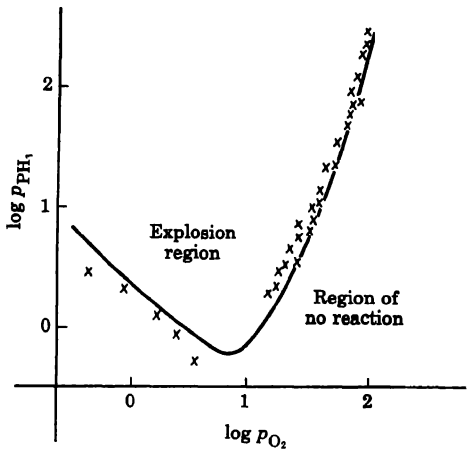


Fig. 5-3. Critical pressures for the oxidation of phosphine by oxygen. The curve represents theory, and the points experimental data. Pressures in mm. of Hg.

tion of phosphine has the same form as equation 4-4. This equation for mixtures of phosphine and oxygen is given below.

$$p_{O_2}{}^{l} p_{PH_3} \left[1 + \frac{\mu p_x}{p_{O_2}{}^{l} + p_{PH_3}} d^2 \right] = k_1 \qquad (5\text{-}10)$$

The constant k_1 in the case of phosphine is about 2×10^3 times greater than

[45] R. H. Dalton and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A125**, 294 (1929); R. H. Dalton, *ibid.*, **A128**, 263 (1930); C. N. Hinshelwood and K. Clusius, *ibid.*, **129**, 589 (1930); H. W. Melville and H. L. Roxburgh, *J. Chem. Phys.*, **2**, 739 (1934); *Nature*, **131**, 690 (1933); M. Trautz and W. Gabler, *Z. anorg. u. allgem. Chem.*, **180**, 321 (1929); H. W. Melville, *Trans. Faraday Soc.*, **28**, 308 (1932); *Proc. Roy. Soc. (London)*, **A138**, 374 (1932); *ibid.*, **139**, 541 (1933); H. W. Melville and H. L. Roxburgh, *J. Chem. Soc.*, **1934**, 264; S. C. Gray and H. W. Melville, *Trans. Faraday Soc.*, **31**, 452 (1935); P. S. Shantarovich, *Acta Physicochim. U.R.S.S.*, **6**, 65 (1937). Also see N. N. Semenov, *Problemy Kinetiki i Kataliza, Sbornik Trudow Konferentsii Posvyashchennoi Sorokaletyu Perekisnoi Teorii Bakha-Englera*, **4**, 46 (1940); *Khim. Referat. Zhur.*, **4**, No. 1, 16 (1941); H. J. Emeléus, *J. Chem. Soc.*, **127**, 1362 (1925).

for phosphorus. This means that in the oxidation of phosphine, the amount of branching is less than in the corresponding phosphorus reaction. Inert gases (such as hydrogen, neon, carbon dioxide, and sulfur dioxide) reduce the lower limit by impeding chain diffusion to the walls, when the pressure of the inert gas is less than that of the phosphine or oxygen. On the other hand, ethylene, benzene, carbon tetrachloride, and tetramethyllead all raise the lower limit. Ultraviolet light reduces the lower limiting pressure of oxygen, due to the formation from phosphine of a substance (atomic hydrogen?) active in the chain reaction.

The upper limiting pressure of oxygen in the oxidation of phosphine is found to be independent of the size of the containing vessel and to decrease slightly in the presence of an inert gas, just as in the case of phosphorus. However, the dependence of the upper limiting pressure of the oxygen upon the pressure of phosphine is different from the case of P_4 vapor in that it is proportional to the square root of the pressure of phosphine at low phosphine pressures and finally becomes relatively insensitive to changes in the phosphine pressure.

It has been found that a cloud which is luminous in the dark and conducts electricity forms in phosphine-oxygen mixtures just before explosion occurs. This action is similar to the "glow" observed in the oxidation of phosphorus. Although details of the chemical reactions involved in the chain mechanism have not been completely worked out, the two following reactions have been suggested as important steps in the over-all process.

$$O + PH_3 \longrightarrow PH + H_2O \qquad (5\text{-}11)$$

$$PH + O_2 \longrightarrow HPO + O \qquad (5\text{-}12)$$

Oxidation of phosphine has been studied above the upper explosion limit of oxygen pressure and found to be a chain reaction which is inhibited by oxygen. Reaction in this region must be artificially induced. This was done photochemically by irradiation with ultraviolet light. The oxidation process below the lower explosion limit has also been studied. In this case, reaction was induced by ignition of the phosphine-oxygen mixture on a heated filament. The photochemical decomposition of deuterated phosphine has been studied.[46] The reaction processes were found to be identical, but the quantum yield for the decomposition of PD_3 is slightly greater (1.10 ×) than that for PH_3.

The products obtained from the reaction between phosphine and oxygen consist of the various oxyacids of phosphorus plus water. Under various

[46] H. W. Melville, J. L. Bolland, and H. L. Roxburgh, *Proc. Roy. Soc.* (*London*), **A160**, 406 (1937).

conditions hypophosphorous, phosphorous, and the various phosphoric acids have been found.[47] Similar products are isolated in the case of the reaction[48] between phosphine and water under pressure at elevated temperatures, except, of course, that hydrogen is formed instead of water.

The catalytic oxidation of phosphorus with oxygen has been studied in a rather fundamental manner by investigating the adsorption of phosphine and oxygen on activated carbon (sometimes containing added copper compounds) and the reaction between the two gases in the adsorbed layer.[49] Occasional other studies on the adsorption of phosphine have also been reported.[50]

Phosphine reacts with heated sulfur to give H_2S and a solid product which appears to be a mixture of the various sulfides of phosphorus.[51] H_2S and PH_3 also react, but considerably more slowly than do PH_3 and sulfur. The reaction of hydrogen sulfide with phosphine results in hydrogen and the phosphorus sulfides. In general, oxidizing agents act on phosphine to give either elemental phosphorus or some reaction product of phosphorus, such as the oxyacids or sulfides. As described in Chapter 4, phosphine reacts with solutions of metal salts to give metal phosphides which in some cases are further reduced by the phosphine to the free metal. The interaction[52] between phosphine and the phosphorus trihalides gives, among other products, elemental phosphorus and the acid HX. On the other hand, phosphine reduces the pentahalides to the trihalides plus HX, as symbolized by the following equation:

$$3\ PCl_5 + PH_3 \longrightarrow 4\ PCl_3 + 3\ HCl \qquad (5\text{-}13)$$

An attempt to prepare PH_5, analogous to the phosphorus pentahalides, was carried out by bringing gaseous phosphine into contact with atomic hydrogen.[53] However, there was no indication of the formation of a phosphorus hydride containing more hydrogen than PH_3.

[47] H. J. van de Stadt, *Z. phys. Chem.*, **12**, 322 (1893). (The metaphosphorous acid described herein does not exist.) I. N. Bushmakin, A. A. Vvedenskii, and A. V. Frost, *J. Gen. Chem. U.S.S.R.*, **2**, 415 (1932).

[48] I. N. Bushmakin and A. V. Frost, *J. Applied Chem. (U.S.S.R.)*, **6**, 607 (1933).

[49] E. A. Andreev and N. N. Kavtaradze, *Izvest. Akad. Nauk S.S.S.R Otdel. Khim Nauk*, **1952**, 1021; *Problemy Kinetiki i Kataliza, Akad. Nauk S.S.S.R.*, **6**, 293 (1949), *Doklady Akad. Nauk S.S.S.R.*, **60**, 1193 (1948); J. Bastick, *Bull. soc. chim. France*, **1952**, 169; *ibid., Mem. 19*, 169.

[50] For example see W. Lange and G. von Krueger, *Z. anorg. u. allgem. Chem* , **216**, 49 (1933).

[51] L. Delachaux, *Helv. Chim. Acta*, **10**, 195 (1927).

[52] R. Mahn, *Jena Z.*, **5**, 158 (1869); *Z. Chem.*, **5**, No. 2, 729 (1869); A. Stock, *Ber* , **53**, 837 (1920).

[53] K. G. Denbigh, *Trans. Faraday Soc.*, **35**, 1432 (1939). Prof. G. Wittig of Heidelberg has also made numerous unsuccessful attempts to produce PH_5.

Phosphine is an extremely poisonous substance.[54] Even a few parts per million of PH_3 in air will cause serious effects after only several hours' exposure.

Organic Phosphines

There are a number of organic derivatives of phosphine in which one, two, or three of the three hydrogen atoms on the phosphorus are replaced by alkyl or aryl groups. These organic phosphines can be prepared by a number of procedures and, indeed, Kosolapoff[55] lists more than twenty ways of making them. Some of the more important of these preparative methods are listed below:

1. Heating a mixture of an alkyl halide and zinc or zinc oxide with phosphonium iodide in a sealed tube at 100–180°C. for several hours gives a mixture of primary, secondary, and tertiary phosphines as well as their phosphonium salts. After cooling, the primary phosphine can be liberated—along with some by-product PH_3—by addition of water. The secondary and tertiary phosphines are then obtained free by adding alkali; they are separated by fractional distillation.

2. Heating white phosphorus with an aliphatic alcohol for several hours in a sealed tube also results in the formation of the entire series of phosphines plus appreciable amounts of their oxidation products.

3. Reaction of alkyl halides with metal phosphides (especially the alkali metal phosphides) gives substituted phosphines. This reaction can be carried out in liquid ammonia. In this case, the products are not always completely free of nitrogen. A better preparation involves triphenylmethyl sodium with phosphine in ether, with subsequent reaction with the alkyl halide. Depending on the relative proportions of metal to phosphine, the yields of either primary, secondary, or tertiary substituted phosphines can be controlled. This reaction can also be carried out in a stepwise manner by reacting partially substituted phosphine with additional metal and then reacting this with more alkyl halide. An example of a good preparation of this type is shown by the following equations.

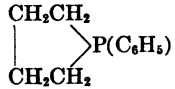
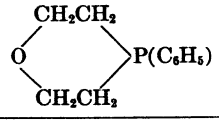
$$(C_6H_5)_3CNa + PH_3 \longrightarrow NaPH_2 + (C_6H_4)_3CH$$
$$NaPH_2 + RX \longrightarrow RPH_2 + NaX \qquad (5\text{-}14)$$

4. Probably the most convenient method for the laboratory preparation of a tertiary phosphine is the interaction of a Grignard reagent with a

[54] M. Loewenthal, *Schweiz. Z. Pathol. u. Bakteriol.*, **12**, 313 (1949); F. Flury and F. Zernik, *Schädliche Gase*, Springer, Berlin, 1931.

[55] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, Chapt. 2, pp. 10–41.

TABLE 5-2
Some Organic Derivatives of Phosphine[55]

Name	Formula	Properties at 25°C.	Melting point (°C.)	Boiling point (°C.)	Remarks
Monomethylphosphine	CH_3PH_2	Colorless gas		−14	Forms crystalline, fairly volatile salts with HCl and HI. Very toxic.
Monophenylphosphine	$C_6H_5PH_2$	Liquid $d_4^{15} = 1.001$	—	160	Not very sol. in H_2O or mineral acids.
Dimethylphosphine	$(CH_3)_2PH$	Liquid	—	21 1	Vapor pres. given by log $p_{mm} = -1370/T + 7\ 539$. All salts with mineral acids are sol. in H_2O.
Diphenylphosphine	$(C_6H_5)_2PH$	Liquid $d_4^{16} = 1\ 07$	—	280	Cryst. salts with HCl and HI decomp. by H_2O
Trimethylphosphine	$(CH_3)_3P$	Liquid	−84 5	37.8	Vapor pres. given by log $p_{mm.} = -1518/T + 7\ 7627$.
Triethylphosphine	$(C_2H_5)_3P$	Liquid $d_4^{15} = 0\ 812$	—	127	
Triphenylphosphine	$(C_6H_5)_3P$	Solid	76	360 (decomp.)	Feebly basic and easily pptd. from soln. in fuming HCl by dilution with H_2O.
Dimethylphenylphosphine	$(C_6H_5)P(CH_3)_2$	Liquid $d_4^{11} = 0\ 968$	—	191	Monohydrochloride is solid; dihydrochloride is liq.
Cyclo-tetramethylenephenylphosphine		Liquid $d_4^{10} = 1\ 050$	—	High (132° at 17 mm. of Hg)	
4-Phenyl-*cyclo*-1-oxa-4-phosphahexane		Solid	136	—	—

phosphorus trihalide or its organic derivative. The reaction is usually conducted in ether and is completed by refluxing

$$PX_3 + 3\,RMgX \longrightarrow R_3P + 3\,MgX_2 \qquad (5\text{-}15)$$

5. It is also possible to make a Grignard reagent of a phosphine itself.[56] A reactive organic halide can then be combined with the phosphine Grignard reagent as shown by the second of the two equations given below:

$$RPH_2 + 2\,R'MgX \longrightarrow RP(MgX)_2 + 2\,R'H$$
$$RP(MgX)_2 + 2\,R''X \longrightarrow RPR_2'' + 2\,MgX_2 \qquad (5\text{-}16)$$

Some physical properties of several typical organic phosphine derivatives are given in Table 5-2. An electron diffraction study has been made of trimethylphosphine,[57] $(CH_3)_3P$, in which it is shown that the P-C distance is equal to 1.87 ± 0.2 A. and that the C—P—C angle is equal to 100 ± 4°. An x-ray[58] study has also been carried out on triphenylphosphine but not to the point where atom-center distances were derived. Molecular weight measurements on the vapor of trimethylphosphine indicates that it is monomeric. The heat of vaporization of this substance is 6.94 kcal., and the variation of its vapor pressure with temperature is given by the following equation.[59]

$$\log p_{\text{mm.}}^{\circ} = -\,1518/T + 7.7627 \qquad (5\text{–}17)$$

Vapor pressure data have also been obtained[60] on dimethylphosphine, $(CH_3)_2PH$. For this compound, the heat of vaporization is 6.27 kcal., and the variation of the vapor pressure with temperature is given by the following equation.

$$\log p_{\text{mm.}} = -\,1370/T + 7.539 \qquad (5\text{-}18)$$

Generally speaking, the organic phosphines are all very reactive substances which possess the characteristic garlic-like odor of phosphine and are probably rather toxic as a class. Certainly the derivatives most closely related to phosphine itself—derivatives such as monomethylphosphine—are extremely toxic.

All organic phosphines undergo oxidation, with the primary and second-

[56] A. Job and G. Dussollier, *Compt. rend.*, **184**, 1454 (1927).

[57] H. E. Springall and L. O. Brockway, *J. Am. Chem. Soc.*, **60**, 996 (1938); for a Raman study of $(CH_3)_3P$, see H. Siebert, *Z. anorg. u. allgem. Chem.*, **273**, 11 (1953).

[58] E. R. Howells, F. M. Lowell, G. Rogers, and A. J. C. Wilson, *Acta Cryst.*, **7**, 298 (1954).

[59] E. J. Rosenbaum and C. R. Sandburg, *J. Am. Chem. Soc.*, **62**, 1623 (1940).

[60] N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316, 718 (1942).

ary phosphines containing the lower aliphatic groups being outstanding in their affinity for atmospheric oxygen. Generally speaking, the aromatic phosphines, especially the triarylphosphines, are relatively stable to atmospheric oxidation at room temperature; but, even these compounds are attacked by a variety of oxidizing agents. Presumably, the air oxidation of all phosphines will exhibit the characteristics of a branching chain reaction. At sufficiently high temperatures, a mixture of triethylphosphine and oxygen shows upper and lower critical pressures and behaves similarly to a mixture of unsubstituted phosphine and oxygen.[61] The lowest oxidation products of the primary phosphines which have been isolated are the phosphonous (also called phosphinic) acids, having the formula $RPH(O)(OH)$; continued oxidation leads to the very stable phosphonic acids, $RP(O)(OH)_2$. The secondary phosphines are usually oxidized to the corresponding dialkylphosphonic (also called phosphinic and phosphonous) acid, $R_2P(O)(OH)$. Tertiary phosphines form phosphine oxides, R_3PO. These tertiary phosphine oxides are crystalline solids which are usually very stable.

Organic phosphines also react very readily with sulfur. Thus, phenylphosphine, $C_6H_5PH_2$, when heated with an equivalent amount of sulfur in an inert atmosphere,[62] gives the compound, $C_6H_5PSH_2$ plus some material with the empirical formula, $(C_6H_5)_3P_3S$. Secondary phosphines add sulfur readily to form polysulfides which, upon treatment with aqueous reagents,[63] give dialkyldithiophosphonic (also known as thiophosphinic and thiophosphonous) acids, $R_2P(S)SH$. Tertiary phosphines add sulfur to give a product similar to the addition product with oxygen. These tertiary phosphine sulfides have the formula, R_3PS.

The organic phosphines also react very vigorously with halogens. Under controlled conditions, hydrogen replacement occurs in the mono- and disubstituted phosphines with the formation of halophosphines (also known as phosphenous chlorides),[64] which are described later in this chapter. Tertiary phosphines add halogens to form the rather unstable dihalides, R_3PX_2 (also discussed later). Although phosphine itself is not basic, the organic phosphines exhibit increasing basic properties with increasing degree

[61] H. W. Thompson and N. S. Kelland, *J. Chem. Soc.*, **1933**, 1231; also see N. Semenoff, *Chemical Kinetics and Chain Reactions*, Clarendon Press, Oxford, 1935, Chapt. VIII, pp. 198–99.

[62] H. Köhler, *Ber.*, **13**, 463 (1880); Thesis, University of Tubingen, Germany, 1877; A. Michaelis and H. Köhler, *Ber.*, **10**, 807 (1877).

[63] A. Cahours and A. W. Hoffman, *Ann.*, **104**, 1, 29 (1857), A. W Hoffman and F. Mahla, *Ber.*, **25**, 2436 (1892); L. Malatesta, *Gazz. chim ital.*, **77**, 509, 518 (1947)

[64] H. C. Brown, *J. Am. Chem. Soc.*, **67**, 503 (1945).

of substitution. Thus, the tertiary phosphines are more basic than are the secondary phosphines which, in turn, are more basic than the primary phosphines. In the parallel case of ammonia and the substituted ammonias, it is correspondingly found that the basicity of monomethylamine is greater than that of ammonia and that the basicity of dimethylamine is greater than that of monomethylamine. However, trimethylamine is a considerably weaker base than dimethylamine. This weakness of trimethylamine is attributed to steric hindrance resulting from the strain introduced in packing three methyl groups around the relatively small nitrogen atom.[64] The phosphorus atom is sufficiently large, however, that this does not occur with increasing substitution of phosphine with methyl groups. Dissociation constants of a number of tertiary phosphine hydroxides have been measured in water-alcohol mixtures.[65] In 50% alcohol solution, the dissociation constants of phenyldialkyl phosphine hydroxides are about 10^{-4}. The basicity of phosphines in water has been roughly correlated with the rate of addition of alkyl halides to tertiary phosphines to give quaternary phosphonium halides.[65]

Complexing of Phosphine and Its Derivatives

Both phosphine and its organic derivatives form a number of addition products with various salts, *e.g.*, boron trifluoride and phosphine react at low temperature to give a product,[66] $H_3P{\cdot}BF_3$, in which the unshared pair of electrons on the phosphorus atom is presumably shared with the boron so that the boron and phosphorus atoms each have eight valence electrons. In this addition compound, both the phosphorus and the boron atoms are probably in sp^3-hybridization, and thus each should exhibit tetrahedral bond symmetry. In addition to the 1.1 complex, there is also a complex with the formula, $H_3P(BF_3)_2$. Boron trichloride and boron tribromide also form 1:1 addition complexes with phosphine. Diborane, B_2H_6, reacts[67] readily with phosphine to give an addition product having the formula, $B_2H_6{\cdot}2PH_3$ or perhaps $H_3B{\cdot}PH_3$. When this product is dissolved in liquid ammonia and the temperature raised to $-60°C.$, phosphine is evolved and a white solid results with the approximate composition, $B_2H_6{\cdot}PH_3{\cdot}NH_3$ which might be a double compound or mixture of $H_3B{\cdot}PH_3$ and $H_3B{\cdot}NH_3$. As would be expected, phosphine also forms complexes with the anhydrous aluminum halides. Thus, $H_3P{\cdot}AlCl_3$, $H_3P{\cdot}AlBr_3$, and $H_3P{\cdot}AlI_3$ have

[65] W. C. Davies and H. W. Addis, *J. Chem. Soc.*, **1937**, 1622.

[66] E. Wyberg and V. Heubaum, *Z. anorg. u. allgem. Chem.*, **225**, 270 (1935); D. R. Martin and R. E. Dial, *J. Am. Chem. Soc.*, **72**, 852 (1950).

[67] E. L. Gamble and P. Gilmont, *J. Am. Chem. Soc.*, **62**, 717 (1940).

been described.[68] Presumably, these compounds are similar to the compounds of phosphine with the boron halides. In other words, phosphorus probably donates a pair of electrons to the aluminum, so that both the phosphorus and aluminum atoms are present as sp^3-hybrids.

In the discussion of metal phosphides given in Chapter 4, it was pointed out that, when phosphine reacts with solutions of certain metal salts, addition compounds of a sort are formed; *e.g.*, phosphine and mercurous chloride react to give a "double salt,"[69] $3\ HgCl_2 \cdot Hg_3P_2$, which can also be written as $P(HgCl)_3$. Presumably, this compound is quite similar to the phosphine-Grignard reagent referred to previously.[56] It should be noted that the reaction product between phosphine and mercurous bromide has a different empirical formula,[70] $2\ HgBr_2 \cdot Hg_3P_2$. In the reaction between phosphine and solutions of silver nitrate, a "double salt" having the formula $3\ AgNO_3 \cdot Ag_3P$ is first formed as an unstable yellow intermediate.[71] The reaction of gaseous phosphine with a number of metal salts to form addition compounds has also been investigated.[72] Typical of these compounds are $CuCl \cdot 2PH_3$ (which readily loses phosphine to form $CuCl \cdot PH_3$), $AgI \cdot PH_3$ (which loses phosphine to give $2\ AgI \cdot PH_3$), $AuI \cdot PH_3$, and $TiCl_4 \cdot PH_3$, as well as $TiCl_4 \cdot 2\ PH_3$.

The organic derivatives of phosphines form addition compounds which are similar to those formed by phosphine itself. Thus, there is an adduct between dimethyl phosphine and boron hydride. The structure of this compound, $(CH_3)_2(H)PBH_3$, has been elegantly proven by a simple straightforward interpretation[73] of the nuclear magnetic resonance spectra of phosphorus, boron, and hydrogen—with proper assignment of the observed resonance peaks in the latter spectrum being facilitated by a simultaneous radiofrequency irradiation at the boron resonance frequency. Both trimethyl- and dimethylphosphine form addition compounds[60] with trimethylaluminum, which is similar to diborane in that it exhibits a dimeric structure, $(CH_3)_3Al \cdot Al(CH_3)_3$.

Vapor-density measurements indicate that the compound formed be-

[68] R. Höltje and F. Meyer, *Z. anorg. u. allgem. Chem.*, **197**, 93 (1931).

[69] L. Moser and A. Brukl, *Z. anorg. u. allgem. Chem.*, **121**, 73 (1922); A. Brukl, *ibid.*, **125**, 252 (1922). The $P(HgCl)_3$ formulation was used by W. E. White and A. H. Bushey, *J. Am. Chem. Soc.*, **66**, 1666 (1944).

[70] P. Lamoult, *Compt. rend.*, **145**, 1175 (1908).

[71] T. Poleck and K. Thümmuel, *Ber.*, **16**, 2435 (1883); *Arch. Pharm.* **22**, No. 3, 1 (1884).

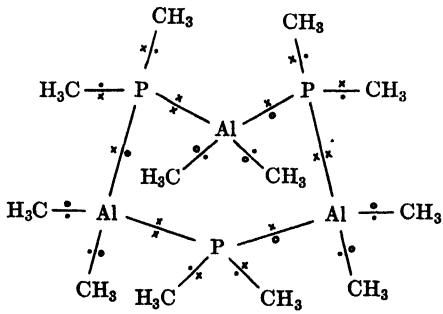
[72] R. Höltje and H. Schlegel, *Z. anorg. u. allgem. Chem.*, **243**, 246 (1940); R. Höltje, *ibid.*, **209**, 241 (1932); R. Scholder and K. Pattock, *ibid.*, **220**, 250 (1934).

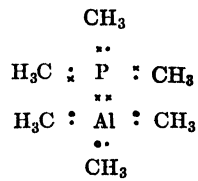
[73] J. N. Shoolery, *Discussions Faraday Soc.*, **19**, 215 (1955).

tween trimethyl phosphine and trimethylaluminum has the formula $(CH_3)_3PAl(CH_3)_3$ and does not dissociate in the vapor at moderate temperatures. The compound formed between dimethylphosphine and trimethylaluminum dissociates in the vapor above 120°C.; below this temperature the density of the vapor corresponds to $(CH_3)_2HPAl(CH_3)_3$. At temperatures above 215°C., mixtures of dimethylphosphine and trimethylaluminum react to form methane and a solid which, if it is homogeneous, is a trimer of the formula $[(CH_3)_2PAl(CH_3)_2]_3$, according to its vapor density.

$$6\,(CH_3)_2PH + 3\,[(CH_3)_3Al]_2 \longrightarrow 6\,CH_4 + 2\,[(CH_3)_2PAl(CH_3)_2]_3 \quad (5\text{-}19)$$

If the logical assumption is made that both the phosphorus and aluminum atoms are present as sp^3-hybrids, the trimeric compound is probably a six-membered ring of alternating phosphorus and aluminum atoms. The electronic structure of this compound and of the adduct between trimethylphosphine and trimethylaluminum is given below:





(5-20)

· = electrons donated by the C atoms
• = electrons donated by the Al atoms
× = electrons donated by the P atoms

} where all electrons are completely equivalent

By means of substitution reactions such as the two shown in equation 5-21, the relative affinities of trimethylaluminum for methyl nitride, phosphide, oxide, and sulfide were obtained. A list of completely methylated compounds in the order of decreasing tendency to form adducts with trimethyl aluminum is: $(CH_3)_3N > (CH_3)_3P > (CH_3)_2O > (CH_3)_2S$. Both of the following reactions are found to proceed nearly quantitatively in the direction of the arrow.

$$(CH_3)_3N + (CH_3)_3P\cdot Al(CH_3)_3 \longrightarrow (CH_3)_3P + (CH_3)_3N\cdot Al(CH_3)_3$$
$$(CH_3)_3P + (CH_3)_2O\cdot Al(CH_3)_3 \longrightarrow (CH_3)_2O + (CH_3)_3P\cdot Al(CH_3)_3 \quad (5\text{-}21)$$

A similar study has been carried out on the more stable addition compounds between organic phosphines and the borines by Burg and associ-

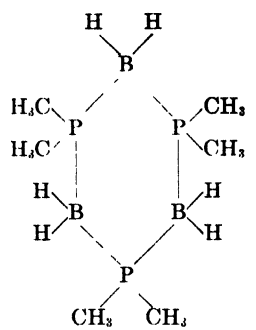
TABLE 5-3
Some Physical Properties of Certain Complexes of the Organic Phosphines

Formula	Boiling point (°C)	Heat of vaporization (kcal.)	Trouton's constant	Constants in vapor pressure equation[a]			Melting point (°C.)	Heat of fusion (kcal./mole)	Molecular weight	
				A	B	State			Measured by vapor density	Calculated from formula
$(CH_3)_2HP:Al(CH_3)_3$	169	11 10	25 2	2429	8 388	l			low	134
$(CH_3)_3P:Al(CH_3)_3$	189	11 8	25 6	2566	8 520	l	62 5		145	148
$[(CH_3)_2P:Al(CH_3)_2]_3$		13 [b]		2933	7 611	s	>220		340	354
$(CH_3)H_2P:BH_3$	150	10 7	25 3	2329	8 400	l	−49 5		62 0	61 9
$(CH_3)_2HP:BH_3$	174	10 7	23 9	2337	8 100	l	−22 6		83	76
$(CH_3)_3P:BH_3$		13 4		2933	9 531	l	103 2		95 4	89 9
$(CH_3)_2HP:BH(CH_3)_2$	Disproportionates	13 1		2857	10 177	l				
$(CH_3)_2HP:B(CH_3)_3$	79	11 8	33 5	2580	10 205	l	−2 8 to −1 8			
$[(CH_3)_2P:BH_2]_3$	235	20 7[b]	26 0	4515	13 10	s	85 5	7 4	234	222
		13 2		2887	8 557	l			214[c]	
$[(CH_3)_2P:BH_2]_4$	310	22 4[b]	25 1	4900	12 28	s	161	8 0	280 5[c]	295
		14 6		3196	8 364	l	334			
$[(CH_3)_2P:B(CH_3)_2]_3$	ca. 334	19 2[b]		4184	9 883	s			334[c]	306

[a] $\log p_{mm.} = -A/T + B$.
[b] Heats of sublimation.
[c] Molecular weights by the Rast camphor method

ates,[74] who are presently very active in developing a rather extensive chemistry of compounds exhibiting P—B bonding. The 1:1 compounds between various methylphosphines and borine or the methylborines are made by simply condensing together the proper phosphine with the proper diborane, *e.g.*, B_2H_6 or $(CH_3)_4B_2H_2$, or borine. The physical properties of a number of adducts obtained by this procedure are given in Table 5-3. In these compounds, the pair of previously unshared electrons on the phosphorus atom are shared with the boron atom so that the boron is no longer in an electron-deficient structure, in which some variety of single electron bond or its equivalent is needed, but assumes an octet of electrons.

The reasonably stable compound, dimethylphosphinoborine, $(CH_3)_2PH \cdot BH_3$, loses hydrogen at 150°C. to form the very stable and chemically resistant trimer, $([CH_3)_2P \cdot BH_2]_3$, and a smaller amount of a tetramer with the same empirical formula. Higher polymers are also produced; but, upon excessive heating, these can be converted to the trimer, which appears to be the most stable member of the series. Presumably, the structure of both the trimer and the tetramer are rings in which the phosphorus and boron atoms—both present as sp^3-hybrids—alternate with each other. The supposed structure formula for the trimer is given below.



(5-22)

The chemical stability of this compound is emphasized by the fact that it hydrolyzes only slowly when heated to 300°C. in a sealed tube with an aqueous solution of hydrochloric acid. The hydrolysis products are 1 mole of boric acid, 1 mole of $H[O_2P(CH_3)_2]$, and 4 moles of hydrogen gas per monomeric unit, $(CH_3)_2PBH_2$. This trimer of dimethylphosphinoborine is also quite stable to pyrolytic decomposition, which starts slowly at tempera-

[74] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953); A. B. Burg, *Abstracts of Papers, 129th Meeting American Chemical Society, Dallas, Texas, April 8–13, 1956*, P4Q. Also see F. G. A. Stone and A. B. Burg, *J. Am. Chem. Soc.*, **76**, 386 (1954). R. E. Florin, L. A. Wall, F. L. Mohler, and E. Quinn, *ibid.*, **76**, 3344 (1954).

tures somewhere around 350°C., with evolution of hydrogen and some methane. At temperatures near 500°C., hydrogen, methane, ethane, and elemental phosphorus have been identified as forming during the first hour of pyrolysis. At the higher temperatures, the ring is destroyed, and the methyl groups are relocated on the boron to give methyl derivatives of the boranes plus elemental phosphorus. In the mass spectra of $[(CH_3)_2P \cdot BH_2]_3$ the migration of methyl groups also occurs, so that at an ionizing potential of 70 v., the major positive ion is $B(CH_3)_2^+$.

The trimer of dimethylphosphinoborine may well be the most stable B—H compound ever obtained as a definite substance.[74] The bonding in this polymer is so strong that it has not been possible to form any dimethylphosphinodiborane by addition of a BH_3 group—in contrast to the easy formation of $(CH_3)_2NB_2H_5$ from $(CH_3)_2NBH_2$. Burg has explained this inertness in terms of π-bonding between the phosphorus and boron atoms in which the electrons of the B—H bond enter hybrid orbitals involving the 3*d*-states of the adjacent phosphorus atoms. This would mean that the electron density on the hydrogen would be lower, so that the protons of acidic solutions would not attack the compound at ordinary temperatures, as is generally the case for compounds in which a B—H link is one of the four bonds to boron.

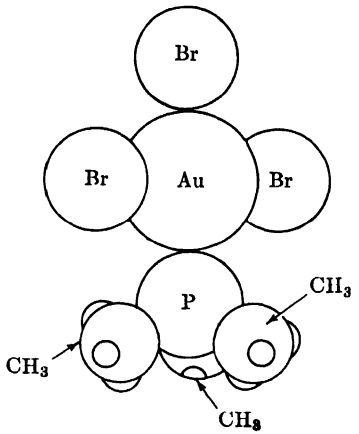
The extreme stability of $[(CH_3)_2PBH_2]_3$ is nearly matched by $[(CH_3)_2PB(CH_3)_2]_3$, which also requires temperatures around 300°C. for hydrolytic breakdown of the P—B bond in aqueous solution. Since the substitution of CH_3 for H on the boron atom is known to lower this atom's acceptor bonding strength very sharply, the π-bond concept appears to be even more necessary here to explain the observed chemistry. In this case π-bonding between the boron and phosphorus atoms more than compensates for the weaker σ-bonding.

In addition to the ring compounds and those based on one phosphorus and one boron atom, there are also a number of higher homologs of the phosphinoborines. The larger compounds occur as mixtures, from thermal treatment of the simpler compounds and from other reactions. These mixtures are usually brittle glasses in which there seems to be considerable crosslinking.

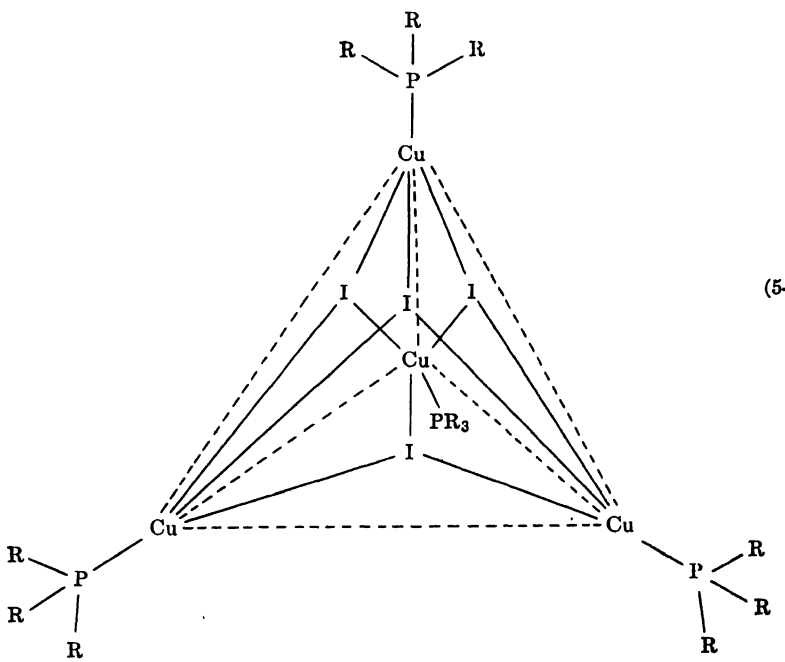
Addition compounds between organic phosphines and metal salts, such as AuCl, have received considerable study.[75] The structures of several of

[75] F. G. Mann and D. Purdie, *J. Chem. Soc.*, **1940**, 1230, 1235; *ibid.*, **1936**, 873; *ibid.*, **1935**, 1549; F. G. Mann, D. Purdie, and A. F. Wells, *ibid.*, **1936**, 1503; J. Chatt and R. G. Wilkins, *ibid.*, **1952**, 273, 4300; *ibid.*, **1951**, 2532; J. Chatt and A. A. Williams, *ibid.*, **1951**, 652; J. Chatt, *ibid.*, **1950**, 2301; K. A. Jensen, *Z. anorg. u. allgem. Chem.*, **229**, 237 (1936).

them have been relatively well worked out. X-ray measurements[76] on the complex between $(CH_3)_3P$ and $AuBr_3$ show that the phosphorus donates a pair of electrons to the gold atom, which then has planar dsp^2-symmetry, as shown below:



(5-23)

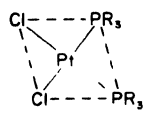


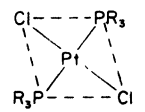
(5-24)

[76] M. F. Perutz and O. Weisz, *J. Chem. Soc.*, **1946**, 438.

Ebullioscopic and cryoscopic measurements on the addition product between the trialkylphosphines and cuprous iodide indicates a four-fold polymerization corresponding to the formula, $(R_3P \cdot CuI)_4$. Since these compounds are isostructural with the addition compound between triethylarsine and cuprous iodide, the structure of which has been obtained from x-ray diffraction studies, the addition products between the trialkylphosphines and cuprous iodide are believed to exhibit the three-dimensional structural formula (5-24) given on the preceding page. In this formula the phosphorus and copper appear to approximate the geometry of sp^3-hybrids, and the iodine has the geometry of an sp^2-hybrid.

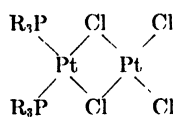
The addition compound between the trialkylphosphines and the dihalides of platinum, palladium, gold, copper, and a number of other metals are of two general types: one having a 2:1 ratio of R_3P to MX_2, the other with a 2:2 ratio. In the case of platinum chloride, these compounds are $2\ R_3P \cdot PtCl_2$ and $R_3P(PtCl_2)_2PR_3$. The platinum has four bonds in a plane corresponding to dsp^2-bonding, so that there are *cis* and *trans* isomers of the 2:1 addition compound, as shown thus:



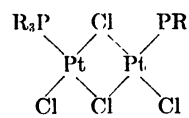


(5-25)

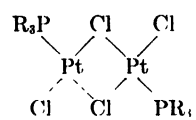
The platinum also exhibits planar symmetry in the 2:2 addition compound, which is formulated as follows:[75]



cis



trans-unsymmetrical

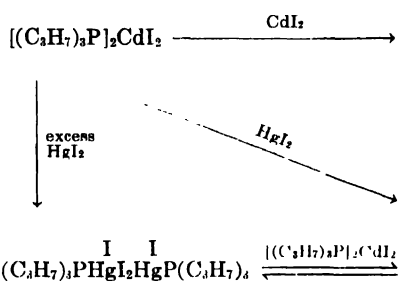


trans-symmetrical

(5-26)

Cis and *trans* isomers have been found for both the monomeric and dimeric compounds of platinum,[75] with the equilibrium in unreactive solvents being shifted toward the *cis* isomer. Proof of structure is based on isomorphism with other addition compounds of the metal dihalides which have received a complete x-ray analysis. The 2:2 addition compounds have also been shown to have twice the molecular weight of the simplest (1:1) formulation by colligative measurements.

By dissolving the metal complexes of the alkylphosphines in, say, alcohol and then treating them with other salts or an excess of the same salt, displacement reactions occur. This is exemplified by the following set of reactions which has been studied by Mann and Purdie.[75]



(5-27)

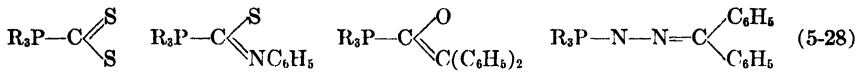
An interesting complexing agent based on phosphines has recently been prepared.[77] This is *P*, *P*, *P'*, *P'*-tetraethylethylenephosphine, $(C_2H_4)_2$-$PCH_2CH_2P(C_2H_5)_2$. Like ethylene diamine, this compound is capable of forming a five-membered chelate ring with a metal ion. Cobalt complexes of the formula $[Co(R_2PCH_2CH_2PR_2)_2X_2]^+X^-$, where X = Cl, Br, or I, were prepared from this compound. The complexes appeared to be of the usual type, with d^2sp^3-bonding of the cobalt. In addition, two other cobalt complexes were described: $[Co(R_2PCH_2CH_2PR_2)_2]^{2+}I_2^-$ and the nonionic $[Co(R_2PCH_2CH_2PR_2)Br_2]$. Physical properties indicated planar dsp^2-bonding of the cobalt in the first of these compounds and tetrahedral sp^3 in the second. Two nickel complexes in which the nickel probably exhibits planar dsp^2-bonding were also prepared. Their formulas are $[Ni(R_2$-$PCH_2CH_2PR_2)X_2]$ and $[Ni(R_2PCH_2CH_2PR_2)_2]^{2+}(ClO_4)_2^-$.

Both phosphine and its organic derivatives form addition products with a number of organic compounds which exhibit π-bonding; *e.g.*, carbon dioxide and phosphine give a white crystalline mass when compressed together in the presence of water.[78] Also, carbon disulfide, water, and phosphine give a crystalline substance when put under pressure at room temperature. Such adducts are very common for the organic phosphines.[55] It is believed that in all of the adducts the phosphorus is present as an sp^3-hybrid.[79] The following formulas have been suggested:

[77] E. Wymore, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1956.

[78] L. Cailletet and L. Bordet, *Compt. rend.*, **95**, 58 (1882).

[79] F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956); also see W. C. Davies and W. P. Watters, *J. Chem. Soc.*, **1935**, 1786 and other references given by Ramirez and Dershowitz.

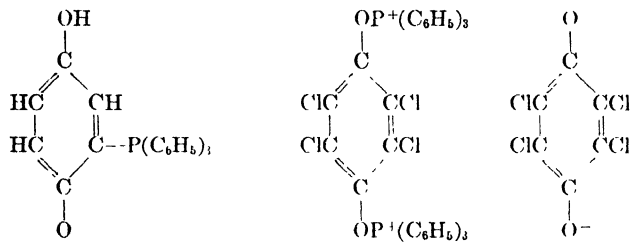


(5-28)

phosphine adduct of carbon disulfide | phosphine adduct of phenylthiocarbimide | phosphine adduct of diphenylketene | phosphine adduct of diazodiphenylmethane

Obviously, there are a number of possible resonance structures which can be written for the above adducts

When tertiary phosphines react with simple quinones, such as *p*-benzoquinone, the hydrogen of a ring carbon is replaced by the phosphorus, whereas, with sterically hindered quinones of high redox potential, such as chloranil, the phosphorus becomes bonded to the oxygen. Formulations of such adducts are given below:

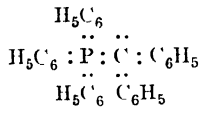


(5-29)

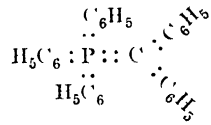
adduct of triphenylphosphine with *p*-benzoquinone | presumably ionic adduct of triphenylphosphine with chloranil

Decomposition of the addition compound between triphenylphosphine and diazodiphenylmethane at 185°C. under vacuum gives a phosphinemethylene having the formula, $(C_6H_5)_3PC(C_6H_5)_2$. This is a red-colored crystalline substance (m.p. 171°C.) which reacts readily with water to give a tertiary phosphine oxide. The simplest electronic configuration of this typical phosphinemethylene indicates an unshared pair of electrons on the methylene carbon atom. However, this unshared electron pair is undoubtedly involved in the formation of a π-bond with the phosphorus wherein the *d*-orbitals of the phosphorus are employed. Presumably, the amounts π-bonding will range from about 0.3 to about 1 0 π-bond per σ-bond, which is the usual amount of π-bonding to be found in phosphorus compounds in which the base σ-bond structure of the phosphorus atom is an sp^3-hybrid. A detailed x-ray analysis of a crystal of a phosphinemethylene would be very desirable—especially if the study were to result in electron density patterns. It would be interesting to see whether the σ-bond base structure of the methylene carbon atom is closer to p^3 (structure 1, below) or sp^2 (structure 2) in its geometric characteristics. Several resonating forms which may

contribute to the structure of triphenylphosphinediphenylmethylene are given below:

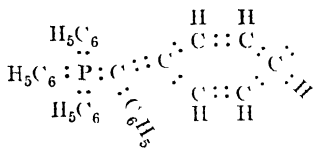


structure 1

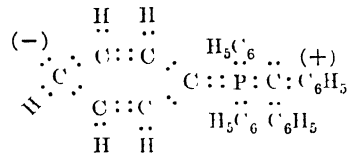


structure 2

(5-30)

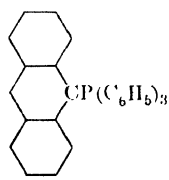


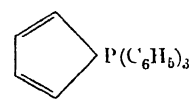
structure 3



structure 4 (three possibilities)

The structures of two interesting related compounds,[80] triphenylphosphinefluorenylidenide and triphenylphosphoninecyclopentadienylide, have been discussed in the recent literature. The ultraviolet absorption spectrum of the latter compound shows considerable conjugation between the unsaturated organic rings.





PHOSPHONIUM COMPOUNDS

Perhaps the best known phosphonium salt is phosphonium iodide, PH_4I, which forms as beautiful, colorless, tetragonal crystals when phosphine and hydrogen iodide are mixed as gases.[81] A more convenient preparation[12] of this compound involves adding iodine to a carbon disulfide solution of white phosphorus, removing the carbon disulfide by volatilization, and then adding the stoichiometric amount of water to give phospho-

[80] L. A. Pinck and G. E. Hilbert, *J. Am. Chem. Soc.*, **69**, 723 (1947); F. Ramirez and S. Levy, *ibid.*, **79**, 67 (1957).

[81] PH_4I was first prepared in this manner by J. J. Houton de la Billardiére, *Ann. chim. et phys.* **6**, No. 2, 304 (1817).

nium iodide and phosphoric acid according to the following equation. The phosphonium iodide is finally purified by sublimation.

$$P_4 + 4\,I_2 \longrightarrow 2\,P_2I_4 \qquad (5\text{-}31)$$

$$10\,P_2I_4 + 13\,P_4 + 128\,H_2O \dashrightarrow 40\,PH_4I + 32\,H_3PO_4 \qquad (5\text{-}32)$$

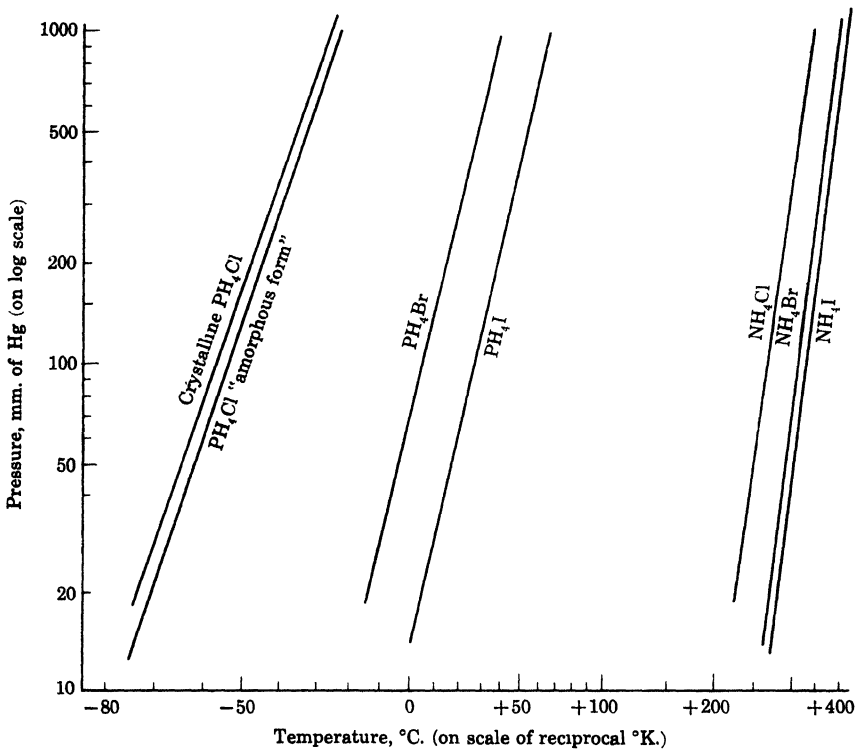


Fig. 5-4 Decomposition pressures of the phosphonium and ammonium halides

Phosphonium bromide and phosphonium chloride are gases at room temperature and 1 atm. pressure. In addition to these three well-known phosphonium halides there appear to be a few other phosphonium salts. Thus, when phosphine is passed into cold (below −10°C.) sulfuric acid, the gas is absorbed without reducing the sulfuric acid; and, at a temperature around −25°C., a white, crystalline, deliquescent solid—believed to be phosphonium sulfate—is formed.[82] Crystalline phosphonium perchlorate, PH_4ClO_4,

[82] A. Besson, *Compt. rend.*, **109**, 644 (1889), A. Stock, W. Böttcher, and W. Langer, *Ber.*, **42**, 2855 (1909).

which was also made at low temperatures, has been described in the literature.[83] As might be expected, phosphonium perchlorate is an extremely explosive compound.

Since phosphonium hydroxide is an extremely weak base (see equation 5-7) and since phosphine is only moderately soluble in water, gaseous phosphine is evolved when a phosphonium halide is added to water or to an alkaline solution. Since the hydrogen halides exhibit a slight partial pressure

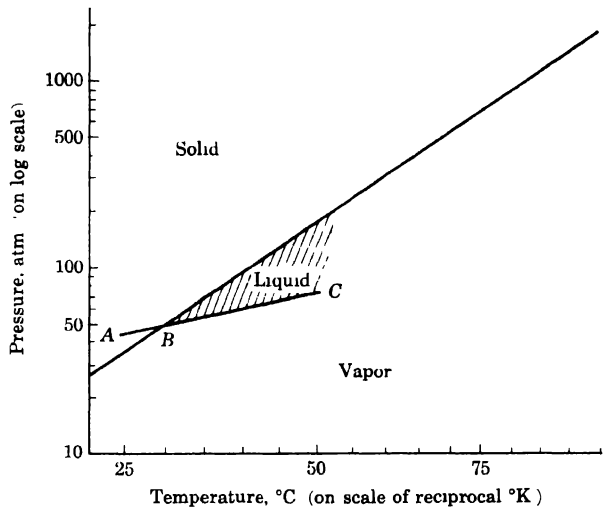


Fig. 5-5 A section of the temperature-pressure diagram for phosphonium chloride. AB = supercooled liquid, B = triple point, C = critical point.

over their aqueous solutions, it is preferable to use an alkali when hydrolyzing phosphonium iodide to make pure phosphine. As is the case with the ammonium halides, the vapors of the phosphonium halides are practically completely dissociated at ordinary pressures according to the reaction given below:

$$PH_4X(s) = PH_3(g) + HX(g) \qquad (5\text{-}33)$$

The decomposition pressures[84] of the three phosphonium halides are compared with those of the equivalent ammonium halides in Figure 5-4, from which it can be seen that the phosphonium salts are considerably more vol-

[83] F. Fichter and H. Arni, *Helv. Chim. Acta*, **17**, 222 (1934).

[84] A. Smith and R. P. Calvert, *J. Am. Chem. Soc.*, **36**, 1363 (1914); F. M. G. Johnson, *ibid.*, **34**, 877 (1912); G. Tammann, *Z. Elektrochem.*, **8**, 158 (1902).

atile than the ammonium salts and that the order of volatility in both series is Cl > Br > I.

One of the phosphonium halides, PH_4Cl, exhibits the rather uncommon phenomenon in which the vapor (which can also be considered as a hypercritical liquid) is in equilibrium with the solid above the critical temperature. This is demonstrated by the diagram[84,85] given in Figure 5-5. It is interesting to note that unlike the ammonium halides, phosphonium iodide does not exhibit a λ-point (or second-order transition) in the curve of its heat capacity *versus* temperature.[86] Since the λ-points obtained for the ammonium halides in the temperature range between −30 and −45°C.

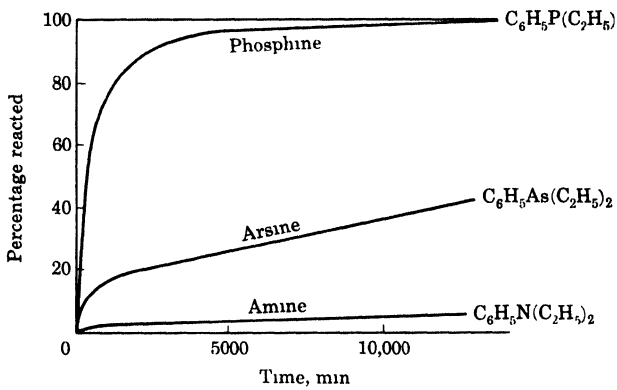


Fig. 5-6. Graph showing the rate of reaction at 35°C in acetone of ethyl iodide with various phenyldiethyl bases to give quaternary compounds.

are attributed to a change from no rotation to free rotation of the ammonium ion in the crystals, it would appear that the phosphonium ion is not free to rotate in phosphonium iodide. Study of phosphonium iodide and chloride crystals by the broad-band nuclear magnetic resonance technique[87] shows that the P-H distance in the phosphonium ion is 1.42 ± 0.02 A. X-ray investigation[87] of phosphonium iodide indicates a close relationship between the atomic arrangement in PH_4I and that of the low-temperature form of NH_4Cl. The Raman spectrum of phosphonium iodide shows fre-

[85] E. Brimer, *J. chim. phys.*, **4**, 267, 476 (1906); *Compt. rend.*, **142**, 1214, 1416 (1906); S. Skinner, *Proc. Roy. Soc.* (London), **42A**, 283 (1887).

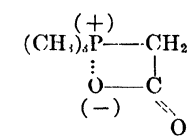
[86] A. Eucken, *Z. Elektrochem.*, **45**, 126 (1939).

[87] L. Pratt and R. E. Richards, *Trans. Faraday Soc.*, **50**, 670 (1954). For x-ray data see L. Coniglio and V. Caglioti, *Rend. accad. sci. Napoli*, **33**, No. 3a, 154 (1927); R. G. Dickinson, *J. Am. Chem. Soc.*, **44**, 1489 (1922).

quencies which have been attributed[88] to the tetrahedral ionic group, PH_4^+.

A number of organic phosphonium salts are described.[89] Of these, the quaternary phosphonium compounds are the most interesting. The simplest and most widely used procedure for making quaternary phosphonium halides is to mix the tertiary phosphine with an alkyl halide and heat the mixture. The rate of the reaction is usually relatively fast as compared to the equivalent rate with tertiary amines and tertiary arsines as shown by Figure 5-6.[90] Presumably, the rate is faster for the phosphine and arsine compounds than it is for the amines because of the formation of an activated complex in which not only the four organic radicals but also the halide is bound covalently to either the phosphorus or arsenic atom through the use of *d*-orbitals. The slower rate of formation of the quaternary arsonium halides as compared to the quaternary phosphonium halide is due to the increasing inertness of the lone pair of electrons when progressing to higher members of a periodic group. To make tetraphenylphosphonium bromide from triphenylphosphine and bromobenzene, aluminum chloride must be used as a catalyst. Apparently the reaction proceeds through the formation of the adduct between the phosphine and aluminum chloride. It should be noted that, in a number of organic reactions, the aluminum chloride adduct has been found to be more reactive than the various phosphines themselves.

With the exception of the hydroxides and alkoxides, the quaternary phosphonium salts are crystalline solids which have a high electrical conductivity in solution and generally exhibit the properties of salts of a strong base. Quaternary phosphonium hydroxides usually occur in the form of hygroscopic, sirupy masses. They exhibit strongly alkaline properties. There is, however, an unusual type of quaternary phosphonium hydroxide which is essentially neutral in solution and which occurs when there is a keto or carboxy group in a position that may give a four-membered or larger ring with the phosphorus atom. This special type of quaternary phosphonium compound, which is often called a phosphobetaine, is exemplified by carboxymethyltrimethylphosphonium hydroxide, the formula of which is given below.



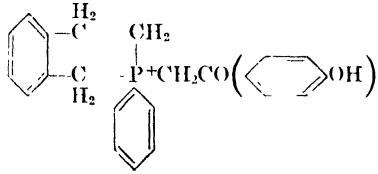
(5-34)

[88] N. Gopal Pal, *Indian J Phys.*, **7**, 285 (1932).

[89] G. M Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, Chapt. 5, pp. 78–97.

[90] W. C. Davies and W. P. G. Lewis, *J. Chem. Soc.*, **1934**, 1599.

Although approximately 25 quaternary phosphonium compounds in which four different radicals are attached to the phosphorus have been prepared,[89] only one of these has been resolved into its optical antipodes.[91] This is 2 - phenyl - 2 - (*p* - hydroxyphenyl) - 1,2,3,4 - tetrahydroisophosphinolinium bromide depicted below. It was resolved as the camphor sulfonate (m.p. 175°C.).



(5-35)

Quaternary ammonium hydroxides having at least one alkyl radical containing two or more carbon atoms undergo thermal decomposition to give an olefin and the trialkylamine according to the equation given below:[92]

$$RCH_2CH_2N^+R'_3 + OH^- \xrightarrow{\Delta} RCH{=}CH_2 + NR'_3 + H_2O \qquad (5\text{-}36)$$

Although similar quaternary phosphonium compounds can undergo the same reaction to some extent, they usually decompose[93] to give a saturated hydrocarbon plus the tertiary phosphine oxide as shown below in equation 5-37. The difference has been ascribed by Ingold to the formation of an activated complex in which the -OH group of the phosphonium hydroxide is bonded directly to the phosphorus by use of the *d*-orbitals of the phosphorus atom. Because the *d*-orbitals for nitrogen occur at unavailably high energies, quaternary ammonium hydroxides can never give amine oxides as decomposition products, according to this mechanism of the process.

$$R_4P^+ + OH^- \rightleftharpoons \underset{\text{activated complex}}{[R_4P(OH)]} \longrightarrow R_3PO + RH \qquad (5\text{-}37)$$

Similarly, Ingold and coworkers[94] found that thermal decomposition of tetraalkyl phosphonium chlorides gave the alkyl chloride plus the tertiary phosphine. However, it should be noted that the early workers[95] reported the formation of olefin as indicated by equation 5-39 given below. The quaternary ammonium chloride always reacts to give the olefin.

[91] F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, **1947**, 1634.

[92] C. K. Ingold and C. C. N. Vass, *J. Chem. Soc.*, **1928**, 3125; W. Hanhart and C. K. Ingold, *ibid.*, **1927**, 997.

[93] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, **1929**, 2342.

[94] G. F. Fenton, L. Hey, and C. K. Ingold, *J. Chem. Soc.*, **1933**, 989.

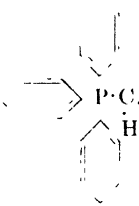
[95] H. Letts and N. Collie, *Phil. Mag.*, **22**, 183 (1886); N. Collie, *ibid*, **24**, 27 (1887), *J. Chem. Soc.* (*London*), **53**, 636, 714 (1888).

$$R_4P^+ + Cl^- \rightleftharpoons \underset{\text{activated complex}}{[R_4PCl]} \xrightarrow{\Delta} R'Cl + R_3P \qquad (5\text{-}38)$$

$$R'CH_2CH_2P^+R_3 + Cl^- \xrightarrow{\Delta} R'CH{=}CH_2 + R_3P + HCl \qquad (5\text{-}39)$$

Reaction[96] to triphenylmethylphosphonium iodide with triphenylmethyl sodium leads to triphenylphosphinemethylene, $(C_6H_5)_3PCH_2$, in which phosphorus has four organic ligands attached directly to it. This reaction and the rapid reaction which occurs when the resulting phosphinemethylene is added to pure water in an inert atmosphere are shown below.

$$[(C_6H_5)_3PCH_3]^+I^- + Na^+[C(C_6H_5)_3]^- \longrightarrow$$



$$+ Na^+I^- + (C_6H_5)_3CH \qquad (5\text{-}40)$$

$$(C_6H_5)_3PCH_2 + H_2O \longrightarrow (C_6H_5)_3P(O)CH_3 + C_6H_6 \qquad (5\text{-}41)$$

Tetraphenylphosphonium chloride is now finding some use as an analytical reagent,[97] since it forms insoluble crystalline salts with the following anions: MnO_4^-, ReO_4^-, TcO_4^-, ClO_4^-, IO_4^-, and BF_4^-, as well as the chloride complexes of a number of multiply charged, heavy metals. A gravimetric procedure has recently been worked out for the tetramethylphosphonium ion,[98] based on precipitation of the chloroplatinate salt. Quaternary phosphonium compounds involving organic radicals of relatively high molecular weight have found some use as disinfectants.[99]

Organic Quasiphosphonium Compounds

There are some organic compounds which can formally be classed as either derivatives of the hypothetical, completely hydrated orthophosphoric acid ($P(OH)_5$ or H_5PO_5) or of the unknown hydroxyphosphonium ion (as in the hydroxide, $[P(OH)_4]^+[OH]^-$). An interesting one of these compounds has the empirical formula[100] $P(OC_6H_5)_5$ and is a very hygroscopic, crystal-

[96] D. D. Coffman and C. S. Marvel, *J. Am. Chem. Soc.*, **51**, 3496 (1929).
[97] H. H. Willard and L. R. Perkins, *Anal. Chem.*, **25**, 1634 (1953).
[98] C. J. Anderson and R. A. Keelar, *Anal. Chem.*, **26**, 213 (1954).
[99] K. Gartner, *Z. Hyg Infektionskrankh.*, **135**, 472 (1952).
[100] L. Anschutz, H. Boedeker, W. Brocker, and F. Wenger, *Ann.*, **454**, 71 (1927), L. Anschutz, F. Koenig, F Otto, and H. Walbrecht, *ibid.*, **525**, 297 (1936).

line solid, melting in the range of 46–52°C. This material is made by reacting phenol with phosphorus pentachloride, usually in two steps, as indicated by the following reactions:

$$3\ C_6H_5OH + PCl_5 \longrightarrow (C_6H_5O)_3PCl_2 + 2\ HCl\ \uparrow \qquad (5\text{-}42)$$

$$(C_6H_5O)_3PCl_2 + 2\ C_6H_5OH \longrightarrow (C_6H_5O)_5P + 2\ HCl\ \uparrow \qquad (5\text{-}43)$$

Dihydroxyphenols, such as catechol,[112] react similarly and yield the corresponding cyclic derivatives. Although they have very little evidence to support their contention, Anschutz and coworkers believe that these compounds exhibit a quasiphosphonium structure; in other words, the pentaphenyl compound probably has the following structure: $[P(OC_6H_5)_4]^+$-$[OC_6H_5]^-$. It should be noted that the molecular weight of this compound, as determined in benzene, was 438 as compared to the theoretical value for an unionized structure of 496. This may indicate some dissociation of the ions, even in benzene. This compound and related compounds, also prepared by Anschutz *et al.*, are soluble in a number of organic solvents and decompose quite rapidly in water to give the appropriate phenol and orthophosphoric acid, $OP(OH)_3$.

A series of related compounds, which are definitely quasiphosphonium salts since a number of different anions have been used in making them, are obtained by reacting amines, such as aniline, with phosphorus pentachloride. An example[101] is the ion $[(C_6H_5NH)_4P]^+$ of which the following crystalline salts have been prepared: chloride (m.p. 275°C.), acetate (m.p. 206–7°C.), propionate (m.p. 240°C.), and sulfate (m.p. 312–13°C.). Other related aromatic derivatives, in addition to the one based on aniline, have been prepared.[101]

In addition to the organic derivatives described above, the tetrahydroxylphosphonium ion, $P(OH)_4^+$, appears to exist in simple form under certain special conditions. The best example of this is the addition compound (m.p. = 47°C.) between H_3PO_4 and $HClO_4$ which forms when the pure acids are mixed.[102] Electrolysis in nitromethane shows that the phosphorus is in the cation, so that the formula of the addition compound is probably $[P(OH)_4]^+[ClO_4]^-$. Naturally, the addition compound decomposes to the constituent acids when dissolved in water. When phosphoric acid is mixed with considerably stronger acids, this formation of $P(OH)_4^+$ in the

[101] M. P. Lemoult, *Compt. rend.*, **136**, 1666 (1903); *ibid.*, **138**, 815 (1904); *ibid.*, **139**, 409 (1904); *ibid.*, **141**, 1241 (1905); *Bull. soc. chim. France*, **35**, 49 (1906); J. E. Gilpin, *Am. Chem. J.*, **19**, 352 (1897); *ibid.*, **27**, 444 (1902).

[102] E. J. Arlman, *Rec. trav. chim.*, **56**, 919 (1937), *ibid*, **58**, 871 (1939); A. Simon and M. Weist, *Z. anorg. u. allgem. Chem.*, **268**, 301 (1952); *Wiss. Z. Hochschule Dresden*, **1**, 293 (1951/52). Also see J. A. Cranston and H. F. Brown, *J. Roy. Tech. Coll*, **3**, 569 (1936) for the $H_3PO_4 \cdot HCl$ complex.

absence of water is apparently a general occurrence, as evidenced by the postulated $P(OH)_4^+Cl^-$ complex.

The phosphonium type of structure has also been attributed to certain organic addition compounds. For example, Mann[41] has given the opinion that the adduct between phosphine oxides, R_3PO, and strong acids, such as HBr, are also ionized, with the phosphorus being in the cation. Thus, we can consider $R_3PO \cdot HBr$ to be $[R_3POH]^+Br^-$, according to this picture.

Mixed phosphonium-quasiphosphonium compounds have also been made. Thus, the compounds $[(C_6H_5O)_3PCH_3]^+I^-$ and $[(C_6H_5O)P(-(C_4H_4)_2(CH_3)]^+I^-$, as well as other derivatives have been obtained by the following general type of reaction:[103]

$$(ArO)_{3-x}PR_x + RX \longrightarrow [(ArO)_{4-x}P(R)_{x+1}]^+ + X^- \qquad (5\text{-}44)$$

where $x = 0$, 1, or 2. A related nitrogen-containing compound[104] is $[(C_6H_5NH)_3P(C_6H_5)]^+Cl^-$. The bromide, iodide, nitrate, and hydroxide of the $[(C_6H_5NH)_3P(C_6H_5)]^+$ cation have been made,[104] in addition to the chloride

LOWER HYDRIDES OF PHOSPHORUS

When phosphine vapors from various sources are passed through a condenser kept at temperatures in the range of -80 to 0°C., a liquid is condensed which has been shown to have the formula P_2H_4 and is variously known as hydrogen hemiphosphide, tetrahydrogen diphosphide, biphosphine, biphosphane, or liquid hydrogen phosphide. This compound has been described in the early literature and is also the subject of two recent investigations.[105,106] Impure calcium phosphide has usually been used to make phosphine from which the biphosphine is condensed. The condensation is often carried out using a trap cooled with dry ice and alcohol, and the crude biphosphine is purified by fractional distillation. Biphosphine boils at 56°C. and freezes at -99°C. The heat of vaporization is 6.89 kcal., and the best vapor pressure data correspond to the following equation.[106]

$$\log p_{\text{mm}} = -1498/T + 7.330 \qquad (5\text{-}45)$$

The vapor density has been measured[105,106,107] by a number of authors and found to agree with the formula, H_4P_2. At 12°C., the liquid has a specific

[103] A. Michaelis and R. Kahne, *Ber.*, **31**, 1048 (1898); A. Michaelis and W. La Coste, *ibid.*, **18**, 2109 (1885).

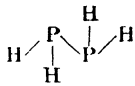
[104] A. Michaelis and F. Kuhlmann, *Ber.*, **28**, 2212 (1895).

[105] P. Royen and K. Hill, *Z. anorg. u. allgem. Chem.*, **229**, 97 (1936).

[106] E. C. Evers, E. H. Street, J. M. Finn, S. Roggenbrug, and D. M. Gardner, *Final Report, Contract No. N8onr-74200, Nonr-598(00)*, University of Pennsylvania, Philadelphia, 1955, E. C. Evers and E. H. Street, *J. Am. Chem. Soc.*, **78**, 5726 (1956).

[107] L. Gattermann and J. W. Hausknecht, *Ber.*, **23**, 1174 (1890). M. Croullebois, *Comm.*

gravity of 1.02. Presumably, the biphosphine molecule has the following structure



(5-46)

Biphosphine decomposes into phosphine plus solid lower hydrides of phosphorus, according to the equation given below

$$(3x - y)\,P_2H_4 \longrightarrow (4x - 2y)\,PH_3 + 2\,P_xH_y \qquad \text{for } x > y \qquad (5\text{-}47)$$

At low temperatures (around −80°C.), this decomposition is quite slow. However, at 0°C. and above, decomposition occurs rapidly—both in the gas and liquid phases. Thus, at 0°C., decomposition in the gas phase becomes detectable within a few minutes. This necessitated placing emphasis on the lower temperature results in obtaining the vapor pressure data given in equation 5-45. At room temperature, liquid biphosphine turns noticeably yellow within the first day after it is made, and during a period of several days thereafter the whole liquid mass gradually solidifies. After standing for a number of days, the solid approaches a limiting composition, the hydrogen content of which can still be reduced by continuously pumping off the phosphine.

The constitution of the solid hydrogen phosphides obtained through the reaction of equation 5-47 has been the subject of several papers.[106,108] These materials are all amorphous yellow solids which have an empirical composition near P_2H, if a sufficient length of time is allowed for removal of the phosphine. Upon mild heating they lose additional phosphine to give reddish solids having such empirical formulas as P_9H_2 and P_5H_2. Strong heating derives off more hydrogen (as PH_3 plus perhaps some H_2). Presumably, identical solid phosphorus hydrides result from a number of processes other than the thermal decomposition of biphosphine. For example, such solid lower hydrides are formed when certain of the metal phosphides are hydrolyzed.[109] In addition, when aluminum phosphide, AlP, is treated with dry hydrogen chloride vapor, the yellow solid phosphorus hydrides are obtained.[110] They are also formed[111] during hydrolysis of P_2I_4 and by reacting[112] white phosphorus with potassium hydroxide in glycerin.

[108] P. Royen, *Z. anorg. u. allgem. Chem.*, **229**, 369 (1936); P. Royen and K. Hill, *Naturwissenschaften*, **24**, 108 (1936), A. Stock, W. Bottcher, and W. Lenger, *Ber.*, **42**, 2839, 2847 (1909); R. Schenck and E. Buck, *ibid.*, **37**, 915 (1904), L. Hackspill, *Compt. rend.*, **156**, 146 (1913).

[109] W. Biltz, I. Mathiesen, and F. W. Wrigge, *Z. anorg. u. allgem. Chem.*, **232**, 284 (1937).

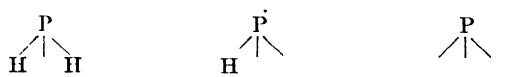
[110] W. E. White and A. H. Bushey, *J. Am. Chem. Soc.*, **66**, 1666 (1944).

[111] J. H. Kolitowska, *Roczniki Chem.*, **15**, 29 (1935).

[112] E. Montignie, *Bull. soc. chim. France*, **8**, 541 (1941).

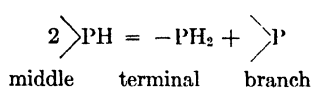
The early workers thought of these materials as simple compounds of relatively low degrees of polymerization. Thus, Schenck and Buck measured the "molecular weight" of a sample having an empirical composition near P_2H in molten yellow phosphorus to get the molecular formula $P_{12}H_6$. Royen has proposed that the solid hydrogen phosphides consist of the sorption product of PH_3 on a form of yellow phosphorus—an extension of an earlier idea of Hackspill, in which he suggested that the hydride with the approximate formula P_2H consisted of a sorption complex of P_2H_4 on the solid $(P_5H_2)x$. It should be remarked that Royen found that the solid hydrides which he investigated were amorphous to x-rays; and presumably all of the solid phosphorus hydrides are amorphous.

The entire body of available experimental data seems to be in accord with the idea that the solid lower hydrides of phosphorus are high polymers, similar in many respects to organic plastics and the phosphate glasses (see Chapter 12 for the detailed theory which should be nearly directly applicable to these phosphorus hydrides). We can conceive of all phosphorus hydrides as being made up of three structural units which are shown below:



(5-48)

Biphosphine consists of two terminal units attached to each other. Presumably, there is a triphosphine and higher members of the series of chain phosphorus hydrides having the generic formula, $P_nH_{(n+2)}$. Members of such a hypothetical series of chain hydrogen phosphides consist of terminal units on either side of a series of middle groups. Obviously, the generic formula $P_nH_{(n+2)}$ also fits phosphine, which is an isolated group from which no other structures can be built. Similarly to the case of the phosphates, there is probably an equilibrium between the various structural units shown above (5-48) and between these groups and phosphine. Such an equilibrium is exemplified by the following equation.



(5-49)

For hydrides in which the H/P mole ratio is less than unity, there must be branching units in the structure, and hence these compounds are probably similar to the three-dimensional polymers described by Flory (see Chapter 12). This means that the solid phosphorus hydrides *at equilibrium* should

consist of a three-dimensional network (equivalent to Flory's "gel phase") in the interstices of which there are smaller structures (Flory's "sol phase") which may be straight chains or exhibit in themselves considerable branching and crosslinking. Obviously, the three-dimensional network cannot be dissolved in any solvent without being destroyed; but it might be possible, working at low temperatures, to extract phosphorus hydrides corresponding to the interstitial material. This could be a way of obtaining phosphorus hydrides of relatively simple structure which are yet more complicated than biphosphine.

From general theory, one would expect a random-reorganization equilibrium corresponding to any given temperature, H/P ratio in the solid, and the concomitant partial pressure of volatile hydrogen phosphides. Since study of hydrogen phosphides is usually carried on at temperatures below about 100°C., the time for reaching equilibrium will be long, and it is very possible that equilibrium may never have been reached by any of the experimenters. However, the work of Evers *et al.* and Stock *et al.* indicates that the solid hydride with an H/P mole ratio of about 0.5 is in equilibrium with an inappreciably small partial pressure of PH_3 at room temperature Further investigations of the composition of solid hydrides should be carried out with the presumed reorganization equilibrium in mind –probably approaching the equilibrium from higher and lower temperatures and higher and lower pressures of phosphine This suggestion is made on the assumption that the rate of attainment of reorganization equilibrium is extremely rapid as compared to the equilibrium with respect to dissociation into the constituent elements. The rate of dissociation of phosphine is discussed on page 189.

The solid hydrogen phosphides are insoluble in all common solvents, including water and alcohol. However, they are soluble in molten phosphorus and diphosphine to some extent, as noted above The solid hydrogen phosphides are reasonably stable in air at room temperature but are easily oxidized by strong oxidizing agents. They can be dispersed in liquid ammonia,[113] with some chemical reaction, to give a colloidal red sol, which upon evaporation leaves a black material which contains some $^1/_2$ to 1 mole of ammonia per mole of phosphorus. A similar reaction in which phosphine is evolved occurs with piperidine to give a black solid of approximately the same composition as obtained by putting the solid hydrogen phosphide in liquid ammonia.

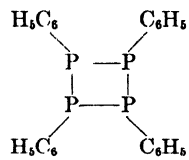
Some organic derivatives of the lower hydrides of phosphorus have been made. Thus, a crystalline tetraphenyldiphosphine (m.p. 67°C.) is said to

[113] A. Stock, W. Bottcher, and W. Langer, *Ber.*, **42**, 2853 (1909).

have been prepared by heating diphenylchlorophosphine with diphenylphosphine,[114] as shown below:

$$(C_6H_5)_2PCl + (C_6H_5)_2PH \xrightarrow{\Delta} (C_6H_5)_2PP(C_6H_5)_2 + HCl \qquad (5\text{-}50)$$

A compound, called phosphobenzene, having the empirical formula C_6H_5P has been described.[115] This yellow powder (m.p. 149°C.) is made by reacting phenyldichlorophosphine with monophenylphosphine in an inert atmosphere. Chlorination of phosphobenzene gives phenyldichlorophosphine, whereas hydrogen chloride regenerates the starting materials. The formula, which corresponds to all middle groups (see equation 5-48 above), and the reasonably low melting point suggests a ring structure, as indicated here for the four-membered ring postulated by Kuchen and Buchwald. This four-membered ring is typical of stable ring structures based on triply connected phosphorus.



(5-51)

Organic derivatives of considerably more complex phosphines and their reactions products have undoubtedly been prepared but left uncharacterized Thus, a yellow, easily oxidizable solid having the empirical composition $(C_6H_5)HP_4$ has been described briefly as being formed, along with other less well defined products, by heating phenyldichlorophosphine with an equimolar amount of water.[116]

PHOSPHORUS HALIDES

The best known of the phosphorus halides are the trihalides and pentahalides. All of the halogens, from fluorine through iodine, form phosphorus trihalides; however, iodine does not form a pentahalide. In addition to the trihalides and pentahalides, iodine and probably chlorine give compounds of the formula P_2X_4; and there are also quite a few polyhalides (primarily involving iodine and bromine) in which there are more than five halogen atoms per phosphorus atom. The formula for the most common

[114] C. Dörken, *Ber.*, **21**, 1505 (1888).

[115] W. Kuchen and H. Buchwald, *Angew. Chem.*, **68**, 791 (1956); A. Michaelis and H. Köhler, *Ber.*, **10**, 807 (1877); also see W. Steinkopf and H. Dudek, *ibid.*, **62**, 2494 (1929) for a 1:1 P-As derivative.

[116] A. Michaelis, *Ber.*, **8**, 499 (1875); A. Michaelis and H. Götter, *ibid.*, **11**, 885 (1878).

variety of polyhalide is PX_7. The best-known phosphorus oxyhalides have the formula POX_3 and are related to the group of sulfohalides having the formula PSX_3. The organic derivatives of phosphorus which are usually considered to be closely related to the inorganic halides of phosphorus are the following: RPX_2, R_2PX, RPX_4, R_2PX_3, R_3PX_2, $RPOX_2$, R_2POX, $RPSX_2$, and R_2PSX. There are also some known compounds in which one or more of the radicals, R, in the above formulations, is substituted by an ester group, OR.

All of the compounds listed in the preceding paragraph will be discussed in the following sections of this chapter. In addition, there are the inorganic fluorophosphates and some organic halophosphates and halophosphites. These are discussed in the appropriate chapters—Chapter 13 in the case of the halophosphates (including the fluorophosphates) and Chapter 7 in the case of the halophosphites. The phosphonitrilic chlorides, $(PNCl_2)_x$, and related structures are discussed in Chapter 6.

In the remainder of this chapter, the trihalides will be treated as a group, as will be the pentahalides, the oxyhalides, the polyhalides, etc. From the viewpoint of phosphorus chemistry, this seems to be a better subdivision than to treat the fluorides, chlorides, bromides, and iodides as separate topics.

SPECTROSCOPIC MOLECULES PX

Investigation of band spectra indicates that phosphorus forms diatomic molecules with the halogens. The molecules PCl, PBr, and PI have been reported.[117] All of these are unstable under normal conditions

PHOSPHORUS TRIHALIDES

Preparation of the Trihalides

Phosphorus trichloride, tribromide, and triiodide are all made by direct union of the elements. If white phosphorus is used, the reaction can be explosively violent. However, the presence of inert solvents, such as is found when white phosphorus is dissolved in carbon disulfide, will slow the reaction, and the use of red phosphorus also allows the reaction to be controlled more readily. In any case, care has to be taken to make sure that the interaction of the elements does not become explosively violent due to the establishment of a branching chain reaction. Phosphorus trifluoride is usually prepared by an exchange reaction between PCl_3 and AsF_3 or SbF_3, using $SbCl_5$ as a catalyst. It can also readily be made by such reactions as

[117] H. G. Howell and G. D. Rochester, *Proc. Unw. Durham Phil. Soc.*, **9**, 126 (1934).

heating copper phosphide with lead fluoride. Details of the preparation of PF_3, PBr_3, and PCl_3 are given in *Inorganic Syntheses*.[118] The preparation of phosphorus trifluoride by exchange of halides between AsF_3 and PCl_3 is an example of a very general type of exchange reaction in which the halogen of lower atomic weight tends to join the counter element of lower atomic weight to give a low-boiling compound which can be fractionated off.[119] An example of this type of reaction is given below:

$$4\,PI_3 + 3\,SnCl_4 \longrightarrow 3\,SnI_4 + 4\,PCl_3\uparrow \qquad (5\text{-}52)$$

Reactions such as the above can be made to proceed strongly to the right by removal of the more volatile constituent

In addition to the pure trihalides, there are several mixed trihalides which have been shown to have distinct structures and are not simply mixtures of the various pure trihalides Long heating of mixtures of the pure trihalides leads to mixed trihalides by an exchange mechanism. The compounds PCl_2Br and $PClBr_2$ have been made[120] by this means as has[121] PF_2Cl and $PFCl_2$. Exchange of halogen atoms between the phosphorus trihalides and other halides has also been employed[122] to produce mixed halides of phosphorus, including PF_2Br and $PFBr_2$. Even before the entire series of mixed trihalides of phosphorus were isolated, they were observed in Raman spectral measurements on previously heated mixtures of the phosphorus trihalides.[123] Indeed, the Raman work has indicated the existence of the compound, PFClBr Although there is some evidence for their formation,[124] the chlorinated phosphines, corresponding to the formulas PH_2X and PHX_2, have not been isolated and purified

[118] C. J. Hoffman, *Inorganic Syntheses*, McGraw-Hill Book Co., New York, 1953, Vol. IV, pp. 149–52 (PF_3); M. C Forbes, C A. Roswell, and R. N. Maxson, *ibid.*, Vol. II, pp. 145–47 (PCl_3). J. F. Gay and R N. Maxson, *ibid.*, Vol II, pp. 147–51 (PBr_3).

[119] T Karantassis, *Compt. rend.*, **182**, 1391 (1926)

[120] A Renc, *Roczniki Chem.*, **14**, 69 (1934), *ibid.*, **13**, 509 (1933); T. Mitobedzki, *Chem. Listy*, **26**, 458 (1932); T Milobedzki and S. Krakowiecki, *Roczniki Chem.*, **8**, 563 (1928)

[121] H. S. Booth and A. R. Bozarth, *J. Am. Chem. Soc.*, **55**, 3890 (1933)

[122] C. J. Wilkins, *J. Chem. Soc.*, **1951**, 2726; H. S. Booth and S. G. Frary, *J. Am. Chem. Soc.*, **61**, 2934 (1939). Also see M. G Raeder, *Z. anorg. u. allgem. Chem.*, **210**, 145 (1933); H. S. Booth and C. F. Winehart, *J. Am. Chem. Soc.*, **54**, 4751 (1932).

[123] O. Theimer, *Acta Phys. Austriaca*, **1**, 188 (1947), F. François and M. L. Delwaulle, *J. chim. phys.*, **46**, 80 (1949); M. L. Delwaulle, *Compt. rend.*, **224**, 389 (1947); *ibid.*, **222**, 1391 (1946); M. L. Delwaulle and F. François, *ibid.*, **223**, 796 (1946); O. Burkard, *Z. physik. Chem.*, **B30**, 298 (1935); B. Trumpy, *Kgl. Norske Videnskab. Selskab. Forh.*, **4**, 102 (1931); *Z. Physik*, **68**, 675 (1931).

[124] P. Royen and K. Hill, *Z. anorg. u. allgem. Chem.*, **229**, 112 (1936).

TABLE 5-4
Structural Data for the Phosphorus Halides[a]

Compound	Atom center distances (A)						Bond angles (degrees)
	P—F	P—Cl	P—Br	P—I	P—O	P—S	<X—P—X
				Triply Connected Phosphorus			
PF_3	1.52 ± 0 04						104 ± 4°
	1 546 ± 0 008						104 ± 3° (assumed)
$PFCl_2$	1 55 ± 0 04	2 02 ± 0 03					102 ± 3°
PCl_3		2 00 ± 0.02					101 ± 2°
		2.03 ± 0 02					100 5 ± 1 5°
PBr_3			2 23 ± 0 01				100 ± 2°
			2 18 ± 0 03				101 5 ± 1 5°
PI_3				2 52 ± 0 01			98 ± 4°
				2 46			100°
				2 43 ± 0 04			102 ± 2°
				Quadruply Connected Phosphorus			
POF_3	1 52 ± 0 02				1 56 ± 0 03		107 ± 2°
	1 52 ± 0 02				**1 45 ± 0 03**		**102 5 ± 2°**
	1.52				**1 48**		
					1 85		**104 ± 3°**
POF_2Cl	1 51 ± 0.03	2 01 ± 0 01			1 55 ± 0 03		106 ± 3°
$POFCl_2$	1.50 ± 0.03	1 99 ± 0 04			1 54 ± 0 03		106 ± 3°
$POCl_3$		2 02 ± 0 03			1 58		106 ± 1°
		1 99 ± 0 02			1 45 ± 0 03		103 6 ± 2°
$POBr_3$			2 06 ± 0 03		1 41 ± 0 07		108 ± 3°

PSF_3	1 51 ± 0 02			1 85 ± 0 02	99 5 ± 2°(F—P—F) 118 ± 2° (F—P—S)
	1 53 ± 0 02			**1.87 ± 0 03**	**100 3 ± 2°** (F—P—F)
	1.53			**1.86**	
$PSCl_3$	2 01 ± 0 02			1 94 ± 0 03	107 (assumed)
	2 02 ± 0 01			**1 85 ± 0 02**	**100 5 ± 1°**
PSF_2Br	1 45 ± 0 08		2 14 ± 0 04	1 87 ± 0 05	106 ± 3°
$PSFBr_2$	1 50 ± 0 10		2 18 ± 0 03	1 87 ± 0 05	100 ± 3°
$PSBr_3$			2 13 ± 0 03	1 89 ± 0 06	106 ± 3°
		Quintuply Connected Phosphorus			
PF_5	1 59 ± 0 03 (apical) 1 57 ± 0 02 (planar) 1 54				See text
PF_3Cl_2	1 59 ± 0 03 (planar)	2 05 ± 0 03 (apical)			See text
PCl_5		2 07 ± 0 05 (apical) 2 01 ± 0 05 (planar) 2 25 (apical) 2.10 (planar)			See text

[a] The majority of the data are from electron-diffraction measurements (see P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950)). The figures given in boldface are from microwave measurements [133,228]

Structure and Properties of the Trihalides

All of the simple phosphorus trihalides, as well as the mixed trihalide, $PFCl_2$, have been studied by electron diffraction.[125] These compounds are typical of those containing triply connected phosphorus atoms in that they exhibit the simple structure shown below.

(5-53)

Detailed data from the electron-diffraction investigations are given in Table 5-4. The crystal structure of phosphorus triiodide has also been investigated by x-ray diffraction;[126] and the atomic positions, insofar as they were obtained, are in agreement with the data from electron diffraction It is interesting to note that crystalline PI_3 is isomorphous with iodoform, HCI_3.

The spectra of the phosphorus trihalides has also received a great deal of attention. Raman spectra of the phosphorus trihalides involving fluorine, chlorine, and bromine have been the subject of considerable investigation.[123,127–129] From this work, frequencies have been assigned[128] to particular bonds and vibrational assignments have been made for individual lines for which the depolarization has also been measured.[127] The infrared spectrum of phosphorus trifluoride has been reported,[130] and the absorption spectra of all three of the phosphorus trihalides have been studied in the ultraviolet region.[131,132] The microwave spectra of PF_3, PCl_3,

[125] O. Hassel and A Sandbo, *Z physik Chem.*, **B41**, 75 (1938), A H Gregg, G C Hampson, G. I Jenkins, P L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, **33**, 852 (1937); L. O. Brockway, *Rev Modern Phys*, **8**, 231 (1936); L. Pauling, L. O Brockway, *J. Am Chem. Soc*, **57**, 2684 (1935), R. Wierl, *Ann. Physik*, **8**, 521 (1931)

[126] H. Braekken, *Kgl. Norske Videnskab. Selskabs Forh*, **5**, 202 (1933)

[127] L. Giulotto, *Nuovo cimento*, **18**, 367 (1941); A. I. Brodskii, A. I. Zak, and L V Korchagin, *Proc Indian Acad. Sci.*, **9A**, 105 (1939); D. M. Yost, *ibid.*, **8A**, 333 (1938), S C. Sirkar and J Gupta, *Indian J. Phys.*, **11**, 55 (1937), A. I. Brodskii and L Korchagin, *Acta Physicochim. U.R S.S.*, **7**, 791 (1937); J B. Howard and E B. Wilson, Jr., *J. Chem. Phys.*, **2**, 630 (1934); D. M. Yost and T. F. Anderson, *ibid*, **2**, 624 (1934), D. M. Yost and J. E. Sherborne, *ibid.*, **2**, 125 (1934).

[128] M. L Delwaulle and F. Francois, *J. chim. phys.*, **46**, 87 (1949)

[129] S. Venkateswaran, *Indian J Phys.*, **6**, 275 (1931).

[130] H. S. Gutowsky and A D Liehr, *J. Chem Phys*, **20**, 1652 (1952), M K. Wilson and S. R. Polo, *ibid.*, **20**, 1716 (1952).

[131] A. D. Walsh, *J. Chem. Soc*, **1953**, 2301, T. Milobedzki and W. Borowski, *Roczniki Chem.*, **18**, 725 (1938); R. H. Potterill and O J. Walker, *Trans. Faraday Soc.*, **33**, 363 (1937); M. V. Vol'kenshtein, *Uspekhi Fiz. Nauk*, **16**, 329 (1936).

[132] M. Jan-Khan and R. Samuel, *Proc Phys. Soc. (London)*, **48A**, 626 (1936).

and PBr_3 have been investigated and interpreted in terms of molecular constants.[133,134] Molecular constants obtained from the microwave investigations are very precise; thus, for phosphorus trifluoride, with an assumed

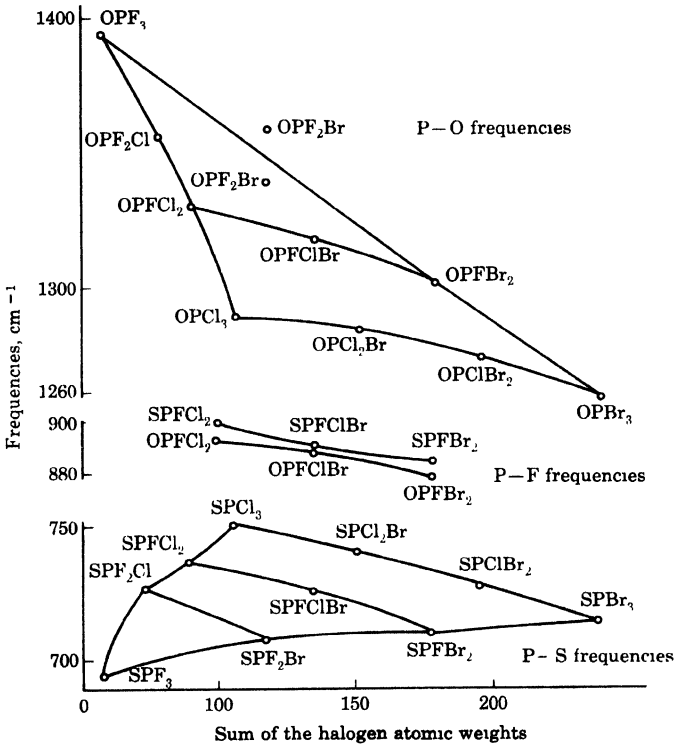


Fig 5-7. Relationships between Raman frequencies observed for some phosphorus halides The two points given for OPF_2Br are due to a Fermi resonance.

< F-P-F = 104 ± 3°, the P-F distance is found to be 1.546 ± 0.008 A., and the dipole moment is found to be 1.025 ± 0.009 debyes.

Before diffraction methods for determining structure were available, a number of cryoscopic measurements were carried out on the phosphorus

[133] P. N. Ghosh, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **87**, 172 (1952), R. G. Shulman, B. P. Dailey, and C. H. Townes, *ibid.*, **78**, 145 (1950); O. R. Gilliam, H. D. Edwards, and W. Gordy, *ibid.*, **76**, 195 (1949); *ibid.*, **75**, 1014 (1949); Q. Williams and W. Gordy, *ibid*, **79**, 225 (1950); P. Kisliuk and C. H. Townes, *ibid*, **78**, 347 (1949), P. Kisliuk, *University Microfilms, Publ. No. 5194*, 83 (1953)

[134] C. M. Johnson, R. Trambarulo, and W. Gordy, *Phys. Rev.*, **84**, 1178 (1951)

trihalides,[135] and these measurements generally indicated a molecular weight corresponding to the simple formula, PX_3. It should also be noted that analysis of a carefully prepared phosphorus trichloride has been used for the determination of the atomic weight of phosphorus.[136] By this procedure, an atomic weight of 31.018 was obtained, this value being 0.14% larger than the presently accepted one.

Some of the more important physical properties of the better known phosphorus trihalides are given in Table 5-1, from which it can be seen that at room temperature PF_3 is a gas, PCl_3 and PBr_3 are liquids, and PI_3 is a solid. As liquids and solids, the trifluoride, trichloride, and tribromide of phosphorus are practically colorless; whereas, the triiodide exhibits a deep red color, due to slight decomposition. Phosphorus tribromide also often has a tan or reddish brown cast.

The viscosity of PCl_3 has been investigated as a function of temperature.[137] When the logarithm of the viscosity is plotted against reciprocal absolute temperature, PCl_3 gives a line which is slightly curved convex to the reciprocal temperature axis. Similar behavior is found for water and $SnCl_4$; however, most liquids (including $POCl_3$) give a straight line on such a plot. The viscosities of mixtures of PCl_3 with ether, benzene, or nitrobenzene also have been studied as functions of temperature and concentration.[138] These mixed systems appear to be ideal, and the viscosities give no indication of compound formation between the constituents.

In addition to the more recent precise work on dipole moments from microwave spectroscopy,[133,134] there are a number of earlier papers in which the dipole moments of the phosphorus trihalides either in vapor form or in solution were measured directly.[139] From ultrasonic measurements,[140] a number

[135] A relatively recent example of cryoscopic molecular weight determinations on PCl_3 and $POCl_3$ in benzene is given by A. R Morgan and S. T. Bowden, *Trans Faraday Soc*, **36**, 394 (1940).

[136] G. P. Baxter and C. J. Moore, *Original Committee 8th Intern Congr. Appl Chem.*, **2**, 21 (1912).

[137] S. T. Bowden and A. R. Morgan, *Phil. Mag*, **29**, 367 (1940); G. P. Luchinskii, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 2116 (1937), G. P. Luchinskii and A. I. Likhacheva, *J. Phys. Chem.* (*U.S S.R.*), **7**, 546 (1936), *J. chim. phys.*, **33**, 488 (1936).

[138] R. G. Rozentreter, *J. Gen. Chem.* (*U.S.S R.*), **2**, 878 (1932); S. Z. Shtamova, *ibid.*, **4**, 240 (1934).

[139] K. Suenaga and A. Kotera, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **70**, 116(1949); U. Grassi, *Nuovo cimento*, **10**, 3 (1933); J. W. Smith, *Proc. Roy. Soc.* (*London*), **A136**, 256 (1932); T. M. Lowry and J Hofton, *J. Chem. Soc.*, **1932**, 207; E. Bergmann and L. Engel, *Z. physik. Chem.*, **B13**, 232 (1931).

[140] A. Weissler, *J. Am. Chem. Soc.*, **71**, 1272 (1949).

of thermodynamic constants such as the adiabatic and isothermal compressibilities have been obtained.

Reactions of the Phosphorus Trihalides

Several interesting radioactive exchange studies have been carried out on the phosphorus trihalides. Exchange between chlorine and PCl_3 and bromine and PBr_3 is rapid in carbon tetrachloride solution.[141] Rapid exchange is also found between PCl_3 and HCl.[142] However, the exchange between P_4 and PCl_3 in carbon disulfide is very slow,[143] of the order of magnitude of weeks as compared to minutes for the halogen exchange. The great difference between these rates is probably due to the fact that chlorine reacts with PCl_3 to give PCl_5, which can play the role of a readily available activated complex in the halide exchange process.

The phosphorus trihalides all undergo hydrolysis when in contact with liquid water or water vapor. The rate of hydrolysis is quite rapid in the case of the triiodide, moderately slow for the trichloride,[144] and even less rapid for the trifluoride, which gives fluorine-containing intermediates.[145] The best-known hydrolysis product is phosphorous acid, the equation for the formation of which is given below:

$$PX_3 + 3\,H_2O \longrightarrow \begin{matrix} O \\ HPO^-H^+ \\ O^- \\ H^+ \end{matrix} + 3\,H^+X^- \qquad (5\text{-}54)$$

In a recent theoretical paper,[146] the hydrolysis of PCl_3 as shown by equation 5-54 is compared with the hydrolysis of NCl_3, which yields HOCl plus NH_3. The very different course of these two reactions is explained by calculation of the energies involved in the various possible routes for the hydrolysis and by showing that the low-energy route is followed in each case.

In addition to the hydrolysis described in equation 5-54, Blaser has shown[147] that a more complicated acid which he calls diphosphorous acid, $H_4P_2O_5$, can also be formed on hydrolysis of phosphorus trichloride and

[141] Ya. A. Fialkov and Y P. Nazarenko, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **1950**, 590; W. Koskoski and R. D. Fowler, *J. Am. Chem. Soc.*, **64**, 850 (1942).

[142] K. Clusius and H. Haimerl, *Z. physik. Chem.*, **51B**, 347 (1942).

[143] P. Muxart, O. Chalvet, and P. Daudel, *J. chim. phys*, **46**, 373 (1949).

[144] G. Carrara and I. Zoppelari, *Gazz. chim. ital*, **26**, 493 (1896).

[145] E. Moissan, *Compt. rend*, **100**, 273 (1885); *Ann. chim. phys.*, **6**, 449 (1885).

[146] A. E. Remick, *J Org Chem.*, **7**, 534 (1942).

[147] B. Blaser, *Ber.*, **68B**, 1670 (1935); *Chem. Ber*, **86**, 563 (1953). E. Thilo and D. Heinz, *Z. anorg. u. allgem. Chem.*, **281**, 303 (1955). For similar data not properly interpreted, see A. D. Mitchell, *J. Chem. Soc*, **127**, 336 (1925) and J. H. Kolitowska, *Z. anorg. u. allgem. Chem.*, **230**, 310 (1937).

phosphorus tribromide, as indicated below. In the presence of strong mineral acids, the diphosphorous acid undergoes additional hydrolysis to form phosphorous acid.

$$2\ PX_3 + 5\ H_2O \longrightarrow H^+\ \begin{matrix} H & O \\ O & P{-}P \\ O & O^- \\ & H^+ \end{matrix} O{-}H^+ + 6\ H^+X^- \qquad (5\text{-}55)$$

As was previously noted, halogenated intermediates are formed in the hydrolysis of phosphorus trifluoride. This action is probably somewhat similar to that observed in the hydrolysis of POF_3, which is described in a following section of this chapter. A simple hypothetical formulation for the intermediate is given in the following equation.

$$PX_3 + 2\ H\ O \longrightarrow \begin{matrix} H \\ OPO \cdot H^+ \\ X \end{matrix} + 2\ H^+X^- \qquad (5\text{-}56)$$

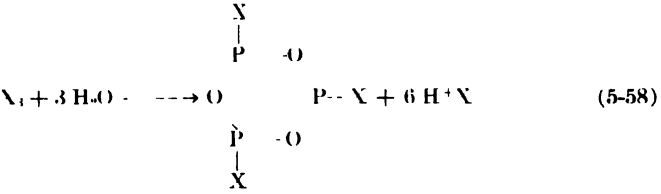
Although halophosphites—such as the monohalophosphorous acid depicted in equation 5-56—have not been isolated and characterized, it is very probable that they exist, at least in the case of the fluoride and perhaps for a short time in the case of the chloride. The "dihalophosphite," $X_2P(O)(H)$, should be a very weak acid, since the tautomeric form in which the hydrogen is attached directly to the phosphorus ought to be present to a much greater extent than the strongly ionized form, $X_2P(OH) \rightleftharpoons H^+ + (X_2PO)^-$.

The discussion of hydrolysis given above pertains primarily to conditions where there was a considerable excess of water. It is known[148] that, when phosphorus trichloride and water are continuously reacted by passing them into molten phosphorous acid, the conditions can be controlled so as to give nothing but orthophosphorous acid and hydrogen chloride, according to equation 5-54. On the other hand, by working at room temperature, Besson[149] was able to make an amorphous, wax-like material which was reported to exhibit the empirical formula, POCl. Probably this was a mixture of a number of different structures, which may have been undergoing random reorganization. Equations for the formation of a typical chain and a typical ring compound of the type which might be found in concentrated mixtures of water and PF_3 or PCl_3 are given below.

$$4\ PX_3 + 3\ H_2O \longrightarrow X{-}\overset{\cdot\cdot}{P}(X){-}O{-}\overset{\cdot\cdot}{P}(X){-}O{-}\overset{\cdot}{P}(X){-}O{-}\overset{\cdot\cdot}{P}(X){-}X + 6\ H^+X^- \qquad (5\text{-}57)$$

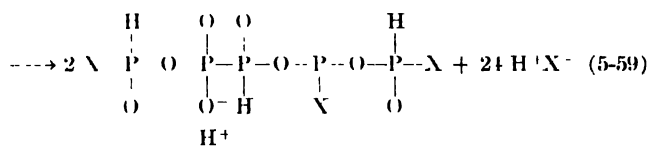
[148] J. W. Lefforge and R. B. Hudson, U. S. Pat. 2,595,198 (1952, assigned to Monsanto Chemical Co.).

[149] A. Besson, *Compt. rend.*, **125**, 771 (1897).



(5-58)

These hypothetical compounds and other similar ones are to be expected when there are approximately equimolar amounts of the trihalide and water. In such concentrated systems it is also conceivable that there will be mixed structures in which part of the phosphorus is connected to four neighboring atoms and part of the phosphorus is connected to three neighboring atoms, as exemplified in the hypothetical equation given below.



(5-59)

Except for the work of Blaser[147] on diphosphorous acid, all of the formulations given above for structures containing more than one phosphorus atom are completely hypothetical. Presumably, additional studies (using modern techniques) of the hydrolysis of the phosphorus trihalides (especially PF_3 and PCl_3) will lead to the verification of a number of complicated structures similar to the ones presented in equations 5-57–5-59. It should be noted that the mixing of phosphorous acid and phosphorus trichloride should lead to essentially the same products if sufficient time is given for reorganization equilibrium to take place. Some exploratory work has already been done on such mixtures.[150]

Under some conditions, the phosphorus trihalides undergo self-oxidation and reduction during hydrolysis. This action appears to be more pronounced with increasing atomic weight of the halogen. With phosphorus triiodide, a yellow solid (perhaps P_2H) is usually formed;[151] and similar

[150] L. Wolf, E. Kalaehne, and H. Schmager, *Ber.*, **62B**, 1141 (1929); also some unpublished work at Monsanto by R. B. Hudson and J. W. Lefforge in which poorly characterized water-white, viscid products were obtained.

[151] B. Corenwinder, *Compt. rend.*, **31**, 172 (1850); *Liebig's Ann. Chem.*, **78**, 76 (1851); *Ann. chim. et phys*, **30**, 242 (1850); A. Besson, *Compt. rend.*, **122**, 140, 814, 1200 (1896); *ibid.*, **124**, 763, 1346 (1897)

yellow solids and other decomposition products can also be obtained by combining PCl_3 and water under certain conditions at elevated temperatures.[152]

The phosphorus trihalides vary considerably in the rapidity with which they react with moist air. Somewhat like phosphine, PF_3 hydrolyzes only slowly in moist air, more rapidly in water, and quite rapidly in alkali; PF_2Cl hydrolyzes slowly in air, whereas $PFCl_2$ does so more rapidly but does not fume. The compounds PF_2Br and $PFBr_2$, both fume in moist air as do PCl_3 and PBr_3. Evidently the reactivity of this group of compounds toward water diminishes as the sum of the atomic numbers of the three attached halogens decreases.

The mixed trihalides of phosphorus show a tendency to decompose spontaneously to the simple trihalides; *e.g.*, PF_2Br decomposes[122] to give PF_3 and $PFBr_2$ plus some PBr_3. As previously mentioned, any mixed trihalide or mixture of simple trihalides can be made to approach equilibrium. A statistically random rearrangement of an equimolar mixture of PX_3 with PY_3 leads to 1:3:3:1 distribution of PX_3, PX_2Y, PXY_2, and PY_3 respectively, at equilibrium.

All of the phosphorus trihalides undergo oxidation quite readily. Phosphorus trifluoride, trichloride, and tribromide readily add chlorine, fluorine, and, in some cases, bromine to form the pentahalides which will be discussed in a following section. When it is pure, phosphorus trichloride rapidly reacts[153] with oxygen to form phosphorus oxychloride, $POCl_3$. However, many impurities, such as iron halides, compounds of sulfur, and rubber, inhibit the reaction. Phosphorus oxychloride can also be made from phosphorus trichloride by reacting it simultaneously with chlorine and water.[154] According to the early literature,[155] sulfur reacts at elevated temperatures with phosphorus trichloride to give $PSCl_3$ and other products. Gaseous hydrogen sulfide was early reported to react with liquid phosphorus trichloride to give phosphorus sulfides and hydrochloric acid.[156] However, dry liquid hydrogen sulfide dissolves phosphorus trichloride, without sign of reaction, to give a solution which is an electrical conductor.[157]

[152] Private communication from R. B. Hudson, Monsanto Chemical Co.

[153] A. F. Isbell and F. T. Wadsworth, *J. Am. Chem. Soc.* (submitted for publication).

[154] A. A. Vanscheidt and V. M. Tolstovyatov, *J. Russ. Phys.-Chem. Soc*, **52**, 270 (1920).

[155] L. Henry, *Ber.*, **2**, 638 (1869).

[156] E. Baudrimont, *Ann. chim. et phys.*, **2**, 5 (1864); G. S. Sérullas, *ibid.*, **42**, 25 (1928)

[157] W. Biltz and E. Keunecke, *Z. anorg. Chem.*, **147**, 171 (1925); G. N. Gaum and J A. Wilkinson, *Proc. Iowa Acad. Sci.*, **32**, 324 (1925).

Addition Compounds of Phosphorus Trihalides

Phosphorus trichloride and boron tribromide combine[158,159] to form $Cl_3P{\cdot}BBr_3$, which is a white solid melting at 42°C. Similar addition products are formed between BBr_3 and PBr_3 and between BCl_3 and PCl_3. In these addition compounds, the originally unshared pair of electrons on the phosphorus trihalide is undoubtedly shared with the boron trihalide. It is interesting to note that a phase study shows that BF_3 and PF_3 do not form an addition product.[160] This seems to indicate that PF_3 is not as good an electron donor as the phosphides of the less electronegative halides.

A number of adducts between the phosphorus trihalides and the halides of metals such as platinum,[161] palladium,[161] gold,[162] copper,[162] chromium,[163] and titanium[164] have been described. Two types of adducts are formed with platinous chloride, $(F_3P)_2PtCl_2$ and $F_3P(PtCl_2)_2PF_3$. The first of these complexes has a square planar configuration about the central platinum atom with the phosphorus trifluoride groups being either *cis* or *trans* to each other. The *cis* isomer predominates when equilibrium between the two is allowed to occur. The other type of complex has a structure in which two platinum atoms are connected by chlorine bridges in a plane, as indicated for the equivalent phosphine complex in equation 5-26. There are three forms—the *cis*, the *trans*-unsymmetrical, and the *trans*-symmetrical isomers, all of which have not been isolated. In these compounds with metal halides, the phosphorus trihalide acts as an electron donor. A series of melting point diagrams of phosphorus trihalides with other halides has been published.[165] These include the following systems: BF_3-PF_3,

[158] D. R. Martin, *Chem. Rev.*, **42**, 581 (1948) gives a review of the coordination compounds of the boron halides.

[159] E. Wiberg and K. Schuster, *Z. anorg. u. allgem. Chem.*, **213**, 94 (1933); A. Stieber, *Compt. rend.*, **195**, 610 (1932); P. Baumgarten and W. Bruns, *Chem. Ber.*, **80**, 517 (1947). Also see J. Tarible, *Compt. rend.*, **132**, 83 (1901) for an unconfirmed report of $Cl_3P{\cdot}2\,BBr_3$.

[160] H. S. Booth and J. H. Walkup, *J. Am. Chem. Soc.*, **65**, 2334 (1943).

[161] J. Chatt and A. A. Williams, *J. Chem. Soc.*, **1951**, 3061; J. Chatt, *Nature*, **165**, 637 (1950); W. Strecker and M. Schurigin, *Ber.*, **42**, 1767 (1909).

[162] M. Levi-Malvano, *Atti accad. naz. Lincei, Mem. Classe sci. fis. mat. e nat., Sez. I* **17**, I, 847 (1910) (Ag); T. L. Davis and P. Aehrlich, *J. Am. Chem. Soc.*, **58**, 2151 (1936) (Cu).

[163] H. S. Fry and J. L. Donnelly, *J. Am. Chem. Soc.*, **40**, 478 (1918); *ibid.*, **38**, 1923 (1916); E. Comanducci, *Chem. Ztg.*, **35**, 706 (1912).

[164] H. Sorum, *Kgl. Norske Videnskab. Selskabs., Forh.*, **17**, 21 (1944); M. G. Raeder, *Kgl. Norske Videnskab. Selskabs. Skrifter*, **1929**, No. 3, 1.

[165] N. A. Pushin and J. Makuc, *Z. anorg. u. allgem. Chem.*, **237**, 177 (1938); *Bull. soc. chim. roy. Yugoslav.*, **9**, 39 (1938). Also see ref. 160 for the BF_3-PF_3 phase diagram.

$AlBr_3$-PBr_3, $SnBr_4$-PBr_3, $SnCl_4$-PCl_3, $AsBr_3$-PBr_3, $SbBr_3$-PBr_3, $AsBr_3$-PBr_5, and S_2Br_2-PBr_5. All of these diagrams show either a smooth melting point curve, such as is obtained with solid solutions, or a simple eutectic with no evidence of compound formation.

A very interesting group of compounds with the formula, $Ni(PX_3)_4$, has recently been prepared.[166] The chlorine derivative is made by reacting phosphorus trichloride with nickel carbonyl, $Ni(CO)_4$. The bromine compound is formed by reacting $Ni(PCl_3)_4$ with PBr, whereas the fluorine derivative is obtained by treating $Ni(PCl_3)_4$ with antimony trifluoride containing a trace of antimony pentafluoride. It is believed that the nickel atom is covalently bonded to the tetrahedrally arranged phosphorus of the trihalides.

Trialkylamines are known to form addition compounds with the phosphorus tri- and pentachlorides Both 1:1 and 3:1 adducts are known between $(C_2H_5)_3N$ and PCl_3.[167] Since both the nitrogen and phosphorus atoms are electron donors, Trost has postulated that the 3*s* electrons of the phosphorus are not involved in bonding, so the phosphorus atom exhibits p^3s-hybridization in R_3NPCl_3 and perhaps p^3d^2s-hybridization in $(R_3N)_3PCl_3$. Presumably, the pair of 3*s* electrons form a completed subvalence shell of electrons, so that the 4*s* orbitals of the phosphorus (which are of lower energy than the 3*d* orbitals, according to Fig 1-2, p. 9) can enter into the hybrid employed in bonding

In addition to the usual reactions involving additions and halogenations, the phosphorus trihalides undergo several unusual reactions with organic compounds. Perhaps the most remarkable of these reactions is the recently discovered oxidative phosphonation of hydrocarbons with phosphorus trichloride first described by Clayton and Jensen in 1948.[153,168] It is found that any hydrocarbon having at least one aliphatically bound hydrogen atom is converted to the corresponding organic phosphoryl dichloride upon being dissolved in phosphorus trichloride and blown with oxygen near room temperature. The reaction appears to be quite nonselective, so that all aliphatically bound hydrogen atoms participate. This means that

[166] J. W. Irvine, Jr. and G. Wilkinson, *Science*, **113**, 742 (1951); G. Wilkinson, *J. Am Chem. Soc.*, **73**, 5501 (1951).

[167] W. R. Trost, *Can. J. Chem.*, **32**, 356 (1954). Also private communication.

[168] J. O. Clayton and W. L. Jensen, *J. Am. Chem. Soc.*, **70**, 3880 (1948); W. L. Jensen and C. R. Noller, *ibid.*, **71**, 2384 (1949); P. Lesfauries and P. Rumpf, *Bull. soc. chim. (France)*, **1950**, 542; R. Graf, *Ber.*, **85**, 9 (1952); L. Z. Soborovskii and Y. M. Zinov'ev, *Zhur. Obshchei Khim.*, **24**, 516 (1954); L. Z. Soborovskii, Y. M. Zinov'ev, and M. A. Englin, *Doklady Akad. Nauk S.S.S.R.*, **67**, 293 (1949); *ibid.*, **73**, 333 (1950); J. R. Eliott, M. Prober, and F. D. George, *Chem Eng News*, **33**, 4512 (1955).

compounds with several such hydrogens, which are not in equivalent positions, yield mixtures of the resulting isomers. Obviously, only substances like cyclohexane or neopentane can yield a simple isomer The yield from this reaction is about 25% calculated on the phosphorus trichloride when equimolar amounts of the hydrocarbon and phosphorus trichloride are used, as indicated in the following equation. Benzene will not undergo this reaction, and phosphorus tribromide cannot be substituted for phosphorus trichloride. The trichloride which does not react with the hydrocarbon (75% and sometimes more) is oxidized to the oxychloride. Light does not affect the yield, which is lowered by the presence of aluminum trichloride and decreased to practically nothing by iodine or sulfuric acid.

$$2\,RH + 2\,PCl_3 + O_2 \longrightarrow 2\,RP(O)Cl_2 + 2\,HCl \qquad (5\text{-}60)$$

Another curious reaction is that of triarylmethyl carbinols with phosphorus trichloride to give[169] the triarylmethylphosphonyl dichloride, $RP(O)Cl_2$, instead of the expected dichlorophosphite, $ROPCl_2$. The reaction probably takes place by means of the following sequence of steps:

$$(C_6H_5)_3COH + PCl_3 \longrightarrow \underset{\text{intermediate adduct}}{(C_6H_5)_3COH\cdot PCl_3} \rightleftharpoons \underset{\text{postulated activated complex}}{[(C_6H_5)_3CP(OH)Cl_3]} \longrightarrow$$

$$(C_6H_5)_3CP(O)Cl_2 + HCl \qquad (5\text{-}61)$$

It is interesting to note that potassium derivatives of the triarylmethyl carbinols undergo the same reaction, in which the C—O bond in the C—O H or C—O —K$^+$ linkage is split

The formation of alkylphosphonyl dichlorides from phosphorus trichloride, the alkyl chloride, and aluminum chloride is also of interest. This reaction[170] takes place in two steps as shown in equation 5-62—the first step being the formation of an addition compound, $(RPCl_3)^+(AlCl_4)^-$, which is similar to the addition compound between PCl_5 and $AlCl_3$, viz. $(PCl_4)^+(AlCl_4)^-$. This organic addition compound is then decomposed by water in the second step of the over-all reaction.

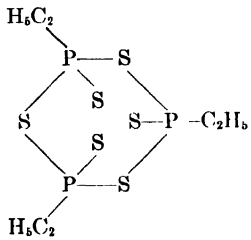
$$PCl_3 + RCl + AlCl_3 \longrightarrow (RPCl_3)^+(AlCl_4)^-$$

$$(RPCl_3)^+(AlCl_4)^- + H_2O \longrightarrow RP(O)Cl_2 + Al^{3+} + 2\,H^+ + 5\,Cl^- \qquad (5\text{-}62)$$

[169] D. R. Boyd and F. J. Smith, *J. Chem Soc.*, **125**, 1477 (1924); *ibid*, **1926**, 2323; D. R. Boyd and G. Chignell, *ibid.*, **123**, 813 (1923); A. E. Arbuzov and B A. Arbuzov, *J. Russ. Phys.-Chem Soc*, **61**, 217 (1929); H. H. Hatt, *J. Chem. Soc.*, **1933**, 776; *ibid.*, **1929**, 2412

[170] A. M. Kinnear and E. A. Perren, *J. Chem. Soc*, **1952**, 3437; J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951) was the first to describe this reaction.

The adducts, $(RPCl_3)^+(AlCl_4)^-$, are either liquids or solids (depending on R) at room temperature. They react slowly with gaseous H_2S at 130°C. with the evolution of HCl The product of this reaction in the case of the ethyl compound is $C_2H_5PS_2$ (m.p. 157°C.), which reacts with warm water to give C_2H_5POS. A possible structure for the $C_2H_5PS_2$ compound is



(5-63)

PHOSPHORUS DIHALIDES

Iodine forms a phosphide which has the empirical formula, PI_2, and a similar compound is reported for chlorine. A considerable amount of work has been done on the iodine compound, but there is only one paper on the chlorine derivative.[171] The diiodide is readily prepared by either fusing together the proper proportions of the constituent elements or reacting iodine with white phosphorus in a solvent such as carbon disulfide[172] or carbon tetrachloride and then cooling to promote crystallization of the diiodide. Study of the kinetics of the reaction between phosphorus and iodine in carbon tetrachloride solution to give phosphorus diiodide shows that the over-all process is a chain reaction which fits the following rate expression.[173] The rate data appear to be in accord with the six reaction steps shown in equation series 5-65.

$$\frac{-d(I_2)}{dt} = \frac{40(P_4)(I_2)^2}{(I_2) - 0.04(P_4)}\left\{1 + \frac{6(P_4)(I_2)}{(I_2) - 0.04(P_4)}\right\} \qquad (5\text{-}64)$$

where the rate is expressed in millimoles/liter/min. It is assumed that a steady state is achieved during the reaction with respect to the concentration of the hypothetical intermediates—P_4I_2, P_2I_2, and P_2. It should be noted that the reaction is affected by light, oxygen, and oxygen-containing solvents, and that the above rate equation and the hypothetical chemical equations (below) involved in the kinetic process refer to the reaction as carried out in the dark at 15°C. under an atmosphere of CO_2.

[171] A. Besson and L. Fournier, *Compt. rend.*, **150**, 102 (1910).
[172] F. E. E. Germann and R. N. Traxler, *J. Am. Chem. Soc.*, **49**, 307 (1927).
[173] D. Wyllie, M. Ritchie, and E. B. Ludlam, *J. Chem. Soc.*, **1940**, 583.

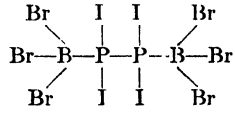
$$\begin{gathered} P_4 + I_2 = P_4I_2 \\ P_4I_2 = P_2I_2 + P_2 \\ P_2I_2 + P_4 = P_4I_2 + P_2 \\ P_2 + I_2 = P_2I_2 \\ P_2I_2 + I_2 = P_2I_4 \\ 2\,P_2I_2 = P_2I_4 + P_2 \end{gathered} \tag{5-65}$$

The phosphorus dichloride was made in small yield by subjecting PCl_3 vapor plus hydrogen to an electrical discharge and isolating the phosphorus dichloride by distillation.

The known physical properties of the two dihalides are given in Table 5-1. Phosphorus diiodide occurs as pale orange colored triclinic crystals. Presumably, the phosphorus dihalides have a formula similar to biphosphine, *i.e.*, X_2PPX_2. This formulation is supported by vapor density determinations on the diiodide which indicate dimerization of the simple formula.[174] However, it is known that phosphorus diioide decomposes readily when melted or vaporized to give phosphorus triiodide and red phosphorus. Therefore, there is some uncertainty with respect to the vapor density measurements, although it was said that decomposition did not occur in an atmosphere of nitrogen under diminished pressure at the temperature (265°C) used in the vapor density study.[174]

Hydrolysis of P_2I_4 in ice water gives[175] a large number of products which include $H_2P(O)(OH)$, $HP(O)(OH)_2$, $OP(OH)_3$, $(HO)_2(O)PP(O)(OH)_2$, PH_3, and P_2H. It has been argued[175] that the presence of $(HO)_2(O)PP(O)(OH)_2$ is an indication that $(PI_2)n$ is dimeric ($n = 2$). However, such hydrolysis data have little or no structural significance, as evidenced by the formation of diphosphorous acid, $(HO)_2(O)PP(H)(O)(OH)$ from PCl_3 on hydrolysis. Although there is no reliable proof, it seems logical, on the grounds of structure theory alone, to assume the dimeric formula for the phosphorus dihalides.

In general, the reactions of phosphorus diiodide are quite similar to those of phosphorus triiodide. It is interesting to note that a complex with boron tribromide has been described.[176] The fact that for each mole of P_2I_4 there are two moles of BBr_3 in the complex is also a very weak argument for the dimerization of the simple formula, PI_2. Presumably, the complex has the following structure:



(5-66)

[174] L. Troost, *Compt. rend.*, **95**, 293 (1882).

[175] J H. Kolitowska, *Roczniki Chem.*, **17**, 616 (1937); *ibid.*, **15**, 29 (1935).

[176] J. Tarible, *Compt. rend.*, **132**, 204 (1901).

PHOSPHORUS PENTAHALIDES

Preparation and Structure of the Pentahalides

Phosphorus pentahalides involving fluorine, chlorine, and bromine are known; but phosphorus pentaiodide has never been isolated, although a number of investigators have attempted to make it. The known phosphorus pentahalides are most readily prepared by reacting the trihalide with the appropriate halogen according to the following equation:

$$PX_3 + X_2 = PX_5 \qquad (5\text{-}67)$$

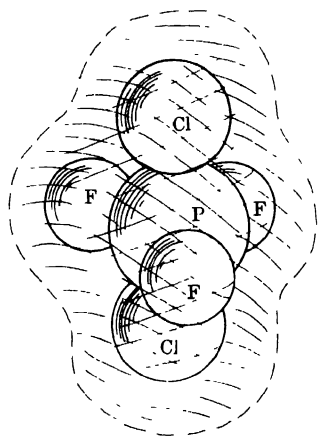


Fig. 5-8 Three-dimensional drawing of the PCl_2F_3 molecule, showing the atoms as spheres exhibiting their covalent radii. The van der Waal radii are shaded in.

This reaction is used quite universally in the preparation of phosphorus pentachloride.[177] Phosphorus pentafluoride is often made in a manner similar to the usual preparation of phosphorus trifluoride by reacting, say, antimony pentafluoride with phosphorus pentachloride. Indeed, the first preparation of phosphorus pentafluoride was carried out by adding arsenic trifluoride drop by drop to phosphorus pentoxide to form a colorless fuming gas and leave arsenic trichloride as the residue.[178] By heating calcium fluoride with phosphorus pentoxide, phosphorus pentafluoride can also be

[177] R. N. Maxson, *Inorganic Syntheses*, ed. by H. S. Booth, McGraw-Hill Book Co., 1939, Vol. I, pp. 99–100.

[178] T. E. Thorpe, *Proc. Roy. Soc. (London)*, **25**, 122 (1877).

formed.[179] Mixed phosphorus pentahalides can be made[120] by combining the pure pentahalides or by adding a halogen to a trihalide based on another halogen.[120] The following mixed pentahalides containing fluorine have been described:[180] PF_3Cl_2, PF_3Br_2, with some evidence of PF_3I_2. The mixed chloride bromides occurring as pentahalides are PCl_3Br_2, PCl_2Br_3, and PCl_4Br.

Electron diffraction studies[181,182] have been carried out on the molecules PF_5, PF_3Cl_2, and PCl_5, and the atom-center distances obtained in this work are reported in Table 5-4. In the vapor state, these molecules are in the form of a trigonal bipyramid, approximating sp^3d-hybridization of the phosphorus atom. In PF_3Cl_2 the two chlorine atoms are in the apical position, with the three fluorine atoms being in the equatorial position, as shown in Figure 5-8. Raman spectra have been interpreted in terms of this model,[183] and theoretical considerations have also been based on it.[184] Nuclear magnetic resonance measurements on the fluorine in PF_5 indicate that, to a first approximation at least, the five fluorines are equivalent and are attached by covalent bonds to the phosphorus, since the fluorine spectrum shows a 1-1 doublet due to spin-spin coupling with the phosphorus.[185] Formulation of the quantum mechanical wave functions for the phosphorus pentahalides offers certain difficulties due to poor overlap of the *d*-orbital contributions to the *s*-*p*-*d*-hybrids. This problem has recently been attacked by introducing a type of polarization by means of which the diffuse *d*-orbitals contract so as to be better suited for covalent bonding based on sp^3d-hybridization of the phosphorus.[186]

Detailed crystal structure studies have been carried out on phosphorus

[179] H. J. Lucas and F. J. Ewing, *J. Am. Chem. Soc.*, **49**, 1270 (1927).

[180] H. Moissan, *Compt. rend.*, **100**, 272, 1348 (1891), *Ann. chim. et phys.*, **6**, 433, 468 (1885) (based on fluorine), A. A. Kuz'menko, *Ukrain. Khim. Zhur.*, **18**, 589 (1952), A. Michaelis, *Ber.*, **5**, 9, 412 (1872); A. L. Stern, *J. Chem. Soc.*, **49**, 815 (1886); M. Prinvault, *Compt. rend.*, **74**, 868 (1872) (chloride-bromides).

[181] L. O. Brockway and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 1836 (1938).

[182] M. Rouault, *Ann. phys.*, **14**, 78 (1940), *Compt. rend.*, **207**, 620 (1938).

[183] H. Siebert, *Z. anorg. u. allgem. Chem.*, **265**, 303 (1951); M. L. Delwaulle and F. François, *J. phys. radium*, **7**, 15 (1946); M. Moureu, M. Magat, and G. Wetroff, *Proc. Indian Acad. Sci.*, **8A**, 356 (1938). Also see R. S. Sharma, *Bull. Acad. Sci. United Provinces Agra and Oudh, India*, **3**, 87 (1933) for the ultraviolet absorption spectrum of PCl_5.

[184] A. Maccoll, *J. Proc. Roy. Soc. N. S. Wales*, **79**, 133 (1946); R. Daudel, A. Bucher, and H. Moureu, *Compt. rend.*, **218**, 917 (1944); H. Moureu, A. M. de Ficquelmont, M. Magat, and G. Wetroff, *ibid.*, **208**, 1579 (1939). Also see ref. 132 for ultraviolet absorption spectra of PCl_5 and PBr_5.

[185] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

[186] D. P. Craig and E. A. Magnussen, *J. Chem. Soc.*, **1956**, 4895.

pentachloride[187] and phosphorus pentabromide.[188] In the crystal, phosphorus pentachloride has an ionic structure corresponding to $(PCl_4)^+(PCl_6)^-$ in which the phosphorus of the cation has the geometry of sp^3-hybridization, and the phosphorus of the anion exhibits sp^3d^2-symmetry. The P-Cl distances in the PCl_4 tetrahedra are equal to 1.97 A., whereas the P-Cl distances in the PCl_6 octahedra are found to be 2.04 A. for the four chlorine atoms in the plane of the phosphorus and 2.08 A. for the two apical chlorine atoms. Phosphorus pentabromide is also ionized in the crystal. However, in this case, the ions are $(PBr_4)^+$ and Br^-. The PBr_4 group is found to be a nearly regular tetrahedron, with the P-Br distances being 2.2 A. For comparison, the shortest distance between the bromide ion and the phosphorus is 4.3 A. It appears from these data that there may be a very small amount of π-bonding in the PCl_4 and PBr_4 tetrahedra, but that there is none in the PCl_6 octahedra, assuming that σ-bond distances do not vary with changes in hybridization.[189]

Pure liquid PCl_5 is a nonconductor of electricity[190] and exhibits a Raman spectrum[191] which has been interpreted on the basis of the trigonal bipyramid structure. This indicates that liquid phosphorus pentachloride is unionized and that the molecule in the liquid has the same structure as in the vapor. However, when phosphorus pentachloride is dissolved in moderately polar solvents, it acts as an electrolyte and undoubtedly is present in ionic form. Transference number experiments indicate that the ions PCl_4^+ and PCl_6^- are formed when PCl_5 is dissolved in nitrobenzene.[192] In such solvents as carbon disulfide or carbon tetrachloride, the amount of ionization is probably small, as shown by conductivity measurements as well as by studies of the dielectric constant.[193]

Physical and Chemical Properties of the Pentahalides

At room temperature, phosphorus pentafluoride vapor has the density[194] corresponding to undissociated PF_5. When compressed to 46 atm. at

[187] D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, **1942**, 642.

[188] M van Driel and C. H. MacGillavry, *Rec. trav. chim.*, **62**, 167 (1943); H. M. Powell and C Clark, *Nature*, **145**, 971 (1940), A. M. de Fiequelmont, G. Wetroff, and H. Moureu, *Compt. rend.*, **211**, 566 (1940).

[189] J R Van Wazer, *J Am Chem. Soc.*, **78**, 5709 (1956).

[190] A. Voigt and W Biltz, *Z anorg. Chem.*, **133**, 277 (1924).

[191] H. Moureu, M. Magat, and G. Wetroff, *Compt. rend.*, **205**, 276 (1937); *ibid.*, **205**, 545 (1937); *ibid.*, **203**, 257 (1936).

[192] D. S. Payne, *J. Chem. Soc.*, **1953**, 1052; V. Gutmann, *Monatsh.*, **83**, 583 (1952).

[193] P. Trunel, *Compt. rend.*, **202**, 37 (1936); J. H. Simons and G. Jessop, *J. Am. Chem. Soc.*, **53**, 1263 (1931).

[194] T. E. Thorpe, *Proc Roy. Soc (London)*, **25**, 122 (1877).

15°C., phosphorus pentafluoride liquefies, and, if the pressure is then partially released, some solid is formed which rapidly returns to the liquid condition. At 125 atm. at the same temperature, the meniscus between liquid and vapor disappears; *i.e.*, the critical point is reached.[195] Thus, with phosphorus pentafluoride it is possible to demonstrate liquefaction, solidification, and critical phenomena of a gas at room temperature. Both vapor pressure and vapor density measurements show that phosphorus pentachloride dissociates in the vapor state according to the following equation,[196,197]

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
$$K_{mm} = p_{PCl_3}p_{Cl_2}/p_{PCl_5} \qquad (5\text{-}68)$$

In the temperature range from 150 to 230°C., the variation of the equilibrium constant with temperature is given by the equation[196]

$$\log K_{mm.} = -20{,}000/(457\ T) + 1.75 \log T + 6.66 \qquad (5\text{-}69)$$

This means that, at the melting point of 160°C., the vapor is 13.5% dissociated. The heat of the dissociation in kilocalories equals (20.0 + 0.00347 T). Dissociation in the vapor, similar to that shown in equation 5-68, is also found for phosphorus pentabromide. However, in the case of phosphorus pentabromide, dissociation equilibrium is attained slowly, so that a number of curious effects are observed during vapor pressure measurements over both the liquid and the solid.[198]

The exchange between radioactive chlorine and phosphorus pentachloride has been measured in carbon tetrachloride solution.[199] The experimental results indicate that three of the chlorine atoms undergo rapid initial exchange, whereas the two chlorine atoms in the apical positions exchange slowly. Furthermore, there does not appear to be a rapid intramolecular exchange between chlorine atoms in the apical and equatorial positions. It is possible that exchange takes place through an activated complex in which a sixth chlorine atom enters into the PCl_5 structure to give four chlorines in the equatorial position, so that the activated complex would correspond to

[195] H. Moissan, *Compt rend*, **99**, 970 (1884), *ibid.*, **101**, 1490 (1885); *ibid*, **102**, 763 (1886), *ibid.*, **103**, 1257 (1886), *ibid*, **138**, 789 (1904), *Bull. soc chim France*, **5**, 454 (1891), *ibid*, **31**, 1004 (1904); *Ann chim et phys*, **8**, 84 (1906).

[196] W Fischer and O. Jubermann, *Z. anorg u. allgem Chem.*, **235**, 337 (1938).

[197] A. Smith, *Z. Elektrochem*, **22**, 33 (1916); A. Smith and R. H Lombard, *J. Am. Chem. Soc.*, **37**, 2055 (1915); A. Smith and R. P. Calvert, *ibid.*, **36**, 1363 (1914); W. Nernst, *Z. Elektrochem*, **22**, 37 (1916); C. Holland, *ibid.*, **18**, 234 (1912); A. Cahours, *Ann. chim. et phys.*, **20**, 369 (1847).

[198] M. van Driel and H. Gerding, *Rec. trav. chim.*, **60**, 869 (1941).

[199] J. Downs and R. E. Johnson, *J. Chem. Phys.*, **22**, 143 (1954).

phosphorus in sp^3d^2-hybridization, rather than the usual sp^3d-hybrid geometry of phosphorus pentachloride.

Phosphorus pentachloride has been employed to a considerable extent as a chlorinating agent in organic chemistry. It also undergoes addition reactions with olefins and aromatic compounds.[200] Preparation of two interesting inorganic compounds from phosphorus pentachloride has been described recently.[201] These are the bis(trichlorophosphazo)sulfone, $O_2S(NPCl_3)_2$, and trichlorophosphazosulfuric chloride, $O_2(Cl)S(NPCl_3)$. Another interesting inorganic derivative of phosphorus pentahalide is the crystalline addition product between phosphorus pentafluoride and nitrogen dioxide,[202] which has the empirical composition $PF_5 \cdot N_2O_4$. Phosphorus pentachloride reacts readily with ammonia to give phosphorus nitrogen compounds which are only poorly characterized. Reports in the literature of phosphorus pentamide, $P(NH_2)_5$, are false. It is possible[203] that the reaction of PCl_5 with an excess of liquid ammonia gives phosphonitrilic amides, $[NP(NH_2)]_n$, corresponding to a substitution of Cl by NH_2 in the phosphonitrilic chlorides described in Chapter 6. With a number of metal fluorides, phosphorus pentachloride reacts[204] to give the metal salt of hexafluophosphoric acid according to the following equation

$$PCl_5 + 6\,MF = MPF_6 + 5\,MCl \qquad (5\text{-}70)$$

With potassium fluoride, an 80% yield of the hexafluorophosphate anion is found.

Phosphorus pentachloride forms a number of addition compounds with the halides of various other elements. A considerable amount of literature[205] has been reviewed recently by Groeneveld,[206] who prepared nearly

[200] For example, G. M. Kosolapoff and J. F. McCullough, *J. Am. Chem. Soc.*, **73,** 855 (1951); B. M. Mikhailov and M. Sh. Promyslov, *Zhur. Obshcheĭ Khim.*, **20,** 338 (1950).

[201] A. V. Kirsanov, *Zhur. Obshcheĭ Khim.*, **22,** 88 (1952), *ibid.*, **22,** 1346 (1952).

[202] A. E. Tassel, *Compt. rend.*, **110,** 1264 (1890).

[203] H. Moureu and P. Rocquet, *Compt. rend.*, **200,** 1407 (1935).

[204] W. Lange and G. von Krueger, *Ber.*, **B65,** 1253 (1932).

[205] R. Weber, *Ann. chim. et phys.*, **107,** 375 (1859), *ibid.*, **132,** 452 (1867), *ibid.*, **125,** 78 (1865); M. E. Baudrimont, *Compt. rend.*, **55,** 363 (1863); *Ann. chim. et phys.*, **2,** 1 (1864), A. W. Cronander, *Bull. soc. chim.*, **19,** 501 (1873); *Ber.*, **6,** 1466 (1873), W. T. Casselman, *Ann.*, **83,** 257 (1852), *ibid.*, **91,** 242 (1854), *ibid.*, **98,** 213 (1856), J. Tuttschiff, *ibid.*, **141,** 111 (1867); R. Metzner, *Ann. chim. et phys.*, **15,** 254 (1898), E. F. Smith and G. W. Sargent, *Z. anorg. Chem.*, **6,** 384 (1894); V. Lenher, *J. Am. Chem. Soc.*, **48,** 1550 (1926); A. E. van Arkel and J. H. De Boer, *Z. anorg. Chem.*, **141,** 289 (1924); E. F. Smith and H. B. Harris, *J. Am. Chem. Soc.*, **17,** 654 (1895); J. M. Matthews, *ibid.*, **20,** 815 (1898).

[206] W. L. Groeneveld, "Chloro- -Onion Verbindungen en Oxy-chloride Solvaten," Thesis, Leiden University, Holland, 1953; *Rec. trav. chim.*, **71,** 1152 (1952); W. L. Groeneveld and A. P. Zuur, *ibid.*, **72,** 617 (1953). Also see paper presented at *Symposium on Coordination Chemistry, Copenhagen,* Aug. 9–13, 1953.

all of the compounds mentioned in the earlier literature and made some new addition compounds. Typical of the compounds are $PCl_5 \cdot BCl_3$ and $PCl_5 \cdot AlCl_3$.

A number of addition compounds of boron trichloride with various chlorides have been investigated,[207] and it is postulated that the ability of a chlorine atom in a compound to act as a donor to the boron atom of boron trichloride is related to the amount of ionic character in the bond holding the chlorine atom in its original molecule. The greater the ionic character in the bond, the stronger the chlorine atom is held by the boron trichloride. Because of the use of *d*-orbitals in its structure, the bonds in phosphorus pentachloride have an unusually high amount of ionic character. Indeed, as was shown in Table 2-7, the heat of formation of either phosphorus pentachloride or phosphorus pentabromide is abnormally low, being equivalent to the energy of approximately four σ-bonds plus five ionic bond contributions.

Some studies have been carried out on the $PCl_5 \cdot AlCl_3$ addition compound in solution.[208] This compound, which is a colorless powder melting at 343°C., is soluble in nitrobenzene and acetonitrile but not in benzene. In nitrobenzene it is a good conductor of electricity. Transference number experiments show that the amount of phosphorus increases in the catholyte and decreases in the anolyte, with the amount of aluminum varying inversely. This means that phosphorus is in the cation and aluminum in the anion, so that the ionic formulation of the addition compound is probably $(PCl_4)^+(AlCl_4)^-$. Similar transference number studies indicate that the $PCl_5 \cdot FeCl_3$ addition compound has a similar ionic structure, $(PCl_4)^+(FeCl_4)^-$. A phase study[196] of the system $AlCl_3$-PCl_5 shows that the melting point of the $PCl_5 \cdot AlCl_3$ adduct (about 380°C.) is above the critical temperatures of both PCl_5 and $AlCl_3$. Moreover, between a PCl_5 mole fraction of 0.5 and 1.0, two immiscible liquid phases are found, one which probably consists primarily of the ionized adduct, $(PCl_4)^+(AlCl_4)^-$, the other primarily of PCl_5.

The addition compounds $PCl_5 \cdot BCl_3$, $PCl_5 \cdot CrCl_3$, $PCl_5 \cdot AuCl_3$, and $PCl_5 \cdot TlCl_3$ appear to be very similar to the aluminum trichloride and iron trichloride adducts with PCl_5. Probably for all of these compounds, the phosphorus is present as a $(PCl_4)^+$ cation, and the metal is in an anion exhibiting the tetrahedral coordinaton corresponding to sp^3-hybridization. There is another series of addition compounds in which the metal

[207] D. R. Martin, *J. Phys. & Colloid Chem.*, **51**, 1400 (1947).

[208] Ya. A. Failkov and Ya. B. Bur'yanov, *Doklady Akad. Nauk S.S.S.R.*, **92**, 585 (1953).

atom probably exhibits the octahedral configuration corresponding to d^2sp^3-hybridization in an anion. This group of compounds includes $3\,PCl_5 \cdot BiCl_3$, $3\,PCl_5 \cdot SbCl_3$ (?), $PCl_5.SbCl_5$, $2\,PCl_5 \cdot SnCl_4$, $2\,PCl_5 \cdot ZrCl_4$, $2\,PCl_5 \cdot TeCl_4$, $PCl_5 \cdot MoCl_5$, $PCl_5 \cdot WCl_5$, and $2\,PCl_5 \cdot PtCl_4$.

There is another group of addition compounds in which it superficially appears that the metal ion is coordinated to five chlorine atoms. This is probably not the case, since x-ray studies[209] on the compounds $(NH_4)_3ZnCl_5$ and Rb_3CoCl_5 show that the ions $(ZnCl_4)^{2-}$ plus Cl^- and $(CoCl_4)^{2-}$ plus Cl^- are present in the respective crystals. Similarly, the crystal lattices of $(NH_4)_2InCl_5\,H_2O$ and $(NH_4)_2FeCl_5 \cdot H_2O$ have been shown[210] to contain the ions $[Cl_5In(OH_2)]^{2-}$ and $[Cl_5Fe(OH_2)]^{2-}$, respectively, in which the metal atoms exhibit the d^2sp^3-octahedral configuration. It is also possible that the structure of the PCl_5 adducts in question may be very involved, having complicated ionic or even perhaps nonionic structures. These adducts are $PCl_5 \cdot SnCl_4$, $PCl_5\,TiCl_4$, $PCl_5 \cdot VCl_4$, and $PCl_5 \cdot SeCl_4$. There are also some PCl_5 adducts in which the metal ion superficially appears to be coordinated with three chlorine atoms. These adducts are $PCl_5 \cdot ZnCl_2$, $PCl_5 \cdot CdCl_2$, and $PCl_5\,HgCl_2$. It is of course conceivable that, in both of these groups of PCl_5 adducts, the PCl_5 donates two chlorine atoms to give a structure which may well be un-ionized. An example of this type of compound is probably found in $PCl_5 \cdot 2BBr_3$.[211]

Although arsenic pentachloride does not exist by itself, it is possible to stabilize this compound as a mixed halide or addition compound with phosphorus pentachloride.[212] Thus, when PCl_5 is combined with $AsCl_3$ and Cl_2, an adduct having the empirical formula $AsPCl_{10}$ is formed. Phosphorus pentachloride also forms adducts with trialkyl amines.[167]

PHOSPHORUS POLYHALIDES

A number of well-crystallized phosphorus halides in which there are seven or more halogen atoms per phosphorus atom have been known for many years. Examples of crystals in which there are seven halogen atoms per phosphorus are PCl_6I, PCl_5BrI, PCl_3Br_4, $PClBr_5I$, PBr_7, and PBr_6I. Examples of crystals in which there are more than seven halogen atoms to each phosphorus are PCl_2Br_7, PCl_3Br_8, PCl_5Br_{10}, PBr_{17}, and PCl_3Br_{18}.

The crystal structure of the phosphorus septahalide, PCl_6I, has been

[209] H. P. Klug and L. Alexander, *J. Am. Chem. Soc.*, **66**, 1056 (1944); H. M. Powell and A. F. Wells, *J. Chem. Soc.*, **1935**, 359.

[210] H P. Klug, E. Kummer, and L. Alexander, *J. Am. Chem. Soc.*, **70**, 3064 (1948).

[211] J. Tarible, *Compt. rend.*, **132**, 83 (1901).

[212] V. Gutmann, *Monatsch.*, **82**, 473 (1951).

investigated by x-ray diffraction.[213] The structure consists of a mixture of symmetrical, tetrahedral $(PCl_4)^+$ ions and linear $(ClICl)^-$ ions. The P-Cl distances are equal to 1.98 A., corresponding to a very small amount of π-bonding in the PCl_4 ion. The I-Cl distance in the anion is 2.36 A., which corresponds rather well to the expected σ-bond length. The com-

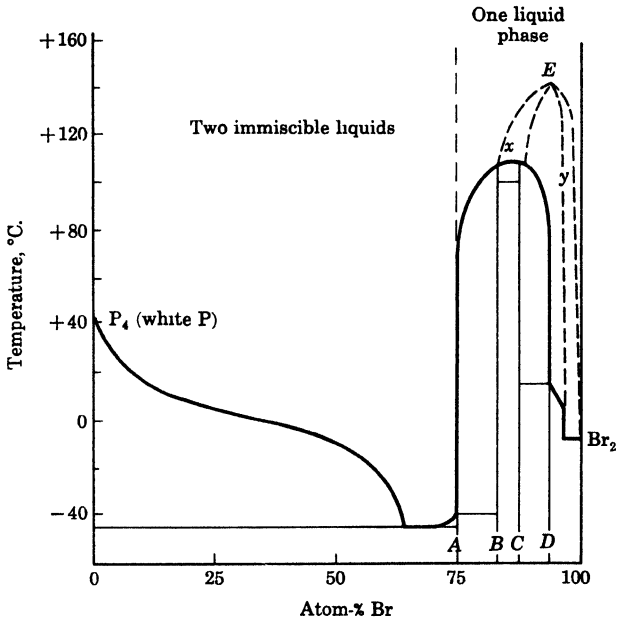


Fig 5-9 The system phosphorus-bromine. A = colorless PBr_3, B = yellow PBr_5, C = red PBr_7, and D = red PBr_{17}. In regions x and y, there are two immiscible liquids which disappear at temperatures above E = 140°C. (93.5 atom-% Br).

pound PCl_6I, called tetrachlorophosphonium dichloroiodide, is isostructural with tetramethylammonium dichloroiodide.

A great deal of study has been carried out on the two-phase systems: phosphorus halide-halogen.[214,215] Of all of these systems, the P—Br system

[213] W. F. Zelezny and N. C. Baenziger, *J. Am. Chem. Soc.*, **73**, 6151 (1952).

[214] Ya. A. Fialkov and A. A. Kuz'menko, *Zhur. Obshcheĭ Khim.*, **22**, 1290 (1952), *ibid.*, **21**, 433 (1951) (PCl_3-Br_2); *ibid.*, **19**, 1645 (1949) (PCl_3-ICl and PBr_3-IBr), *ibid*, **19**, 812 (1949) (PCl_3-I_2, PBr_3-I_2, P_2I_4-I_2, and PCl_5-I_2), *ibid.*, **21**, 473 (1951) (PCl_5ICl and PBr_5-IBr); *ibid.*, **19**, 1007 (1949) (PBr_5-I). For physical properties other than electrical conductivity see *Mem. Inst. Chem., Acad. Sci. Ukr. S.S.R.*, **4**, No. 3, 309 (1937) (PI_3-I_2, viscosity); *ibid.*, **4**, 321 (1937) (PI_3-I_2, densities of liquid).

[215] N. A. Pushin and J. Makuc, *Bull. soc. chim. Belgrade*, **15**, 17 (1950); W. Biltz and K. Jeep, *Z. anorg. u. allgem. Chem.*, **162**, 32 (1927).

has been investigated the most thoroughly.[215] The phase diagram for the P—Br system is given in Figure 5-9, where it can be seen that there are four crystalline compounds: PBr_3, PBr_5, PBr_7, and PBr_{17}. The structures of PBr_3 and PBr_5 have already been discussed. Presumably, PBr_7 has an ionic structure $(PBr_4)^+(Br_3)^-$ or $(PBr_4)^+Br^-(Br_2)$, similar to PCl_6I. The structure of PBr_{17} is unknown, but it may well contain a number of un-ionized Br_2 groups which are present in the lattice in much the same way that water of hydration appears in many crystalline hydrates.

In addition to the phase-diagram studies, there have been some less systematic investigations in which crystalline polyhalides were found.[216] The electrical conductivity in various phosphorus-halogen systems has been extensively studied.[214,217,218] It is interesting to note that in electrolysis of these phosphorus-halogen liquids, the potentials of the anode and cathode are nearly constant over a wide range of current densities from zero upward. This means that the electrodes do not become polarized, probably because the solvent itself (the halogen) acts as a depolarizer. Generally speaking, the conductivity and transference number experiments have been interpreted to show the existence of the PX_4^+ cations and X^- or X_3^- anions. Sometimes two phases occur. Thus, in the system PCl_5-Br_2, phase separation takes place when the PCl_4/Br mole ratio is greater than 0.5. In this case, the upper layer, which is a saturated solution of PCl_3Br_4 in PCl_3, is a nonconductor of electricity as compared to the lower layer, nearly pure PCl_3Br_4, which is a good conductor (7.42×10^{-2} mho/cm for the pure compound at 45°C.) Obviously, the conclusions obtained from electrical measurements on the liquids are in accord with the diffraction data on the crystalline phosphorus halides which have been investigated. Study of the phosphorus polyhalides in solution also gives strong evidence of ionization.[214,219] Thus, spectrophotometric investigation of PCl_6I and PBr_6I re-

[216] I. D. Muzyka and Ya. A. Fialkov, *Doklady Akad. Nauk S.S.S.R.*, **83**, 415 (1952) ($PClBr_6I$ and PCl_5BrI); V. A. Plotnikov and S. I. Yakubson, *Z. physik. Chem.*, **138**, 243 (1928) (PCl_5Br_{10}), M. Primvault, *Compt. rend.*, **74**, 868 (1872) (PCl_2Br_7 and PCl_3Br_8); A. Michaelis, *Ber.*, **5**, 9, 412 (1872); *Z. Chem.*, **7**, 185 (1870), *Jena Z.*, **6**, 290 (1870) (PCl_3Br_8 and others).

[217] V. S. Finkelstein and P. V. Ust'yanova, *J. Phys. Chem. (U.S.S.R.)*, **9**, 773 (1937), V. Finkel'shtein, *Z. physik. Chem.*, **115**, 303 (1925).

[218] V. A. Plotnikov, Ya. A. Fialkov, and V. P. Chalui, *J. Gen. Chem. (U.S.S.R.)*, **6**, 273 (1936) (PI_3-I_2); Y. A. Fialkov, *Acta Physicochim. U.R.S.S.*, **3**, 711 (1935) (PI_3-I_2), V. A. Plotnikov and S. I. Yakubson, *Z. physik. Chem.*, **138**, 235 (1928) (PCl_5-Br_2); V. A. Plotnikov, *Chemistry & Industry*, **42**, 750 (1923); V. A. Plotnikov and V. P. Chalyi, *Mem. Inst. Chem., Acad. Sci., Ukr. S.S.R.*, **3**, 167 (1936) (PI_3-I_2).

[219] A. I. Popov and E. H. Schmorr, *J. Am. Chem. Soc.*, **74**, 4672 (1952); V. Gutmann, *Monatsh.*, **83**, 583 (1952).

veals that these polyhalides dissociate molecularly in carbon tetrachloride solution, as shown by the following equations

$$PCl_6I \rightleftharpoons PCl_5 + ICl \quad (5\text{-}71)$$

$$PBr_6I \rightleftharpoons PBr_5 + Br_2 + IBr \quad (5\text{-}72)$$

However, in the polar solvent, acetonitrile, ionization occurs as shown by the folllowing equation in which X stands for either chlorine or bromine

$$PX_6I \rightleftharpoons PX_4^+ + XIX^- \quad (5\text{-}73)$$

PHOSPHORUS OXYHALIDES

Preparation and Structure

Simple and mixed oxyhalides having the general formula POX_3 are known for fluorine, chlorine, and bromine, but not for iodine Compounds with this formula are variously named as phosphorus oxyhalides, phosphoryl halides, and sometimes as orthophosphoryl halides or phosphorus monoxytrihalides to distinguish them from the other oxyhalides of phosphorus which will be discussed below The phosphorus monoxytrihalides can be prepared by a number of reactions. The simplest one is the oxidation of PCl_3 or PBr_3, which can be carried out by a number of oxygen-donating oxidizing agents, including air.[220] Pure oxygen as well as air reacts rapidly with pure PCl_3.[153] Complete absorption of pure oxygen takes place when the gas rises, as small bubbles, through a depth of 100 cm of the PCl_3. At temperatures between 20 and 50°C., the ability of the liquid to absorb oxygen does not fall off until there is more than 95-97% $POCl_3$ in the PCl_3-$POCl_3$ mixture.[221] Another well-known method for the preparation of phosphorus oxychloride and phosphorus oxybromide is the reaction between phosphorus pentoxide and the phosphorus pentahalide,[222] as shown by the following equation.

$$P_4O_{10} + 6\,PX_5 \longrightarrow 10\,POX_3 \quad (5\text{-}74)$$

In general, reaction of P_2O_5 with any halide gives some POX_3.[223] Thus, sodium chloride and P_2O_5 can be used to make phosphoryl chloride, $POCl_3$; and a number of metallic fluorides have been used with phosphorus pent-

[220] C. R. Johnson and L. G. Nunn, *J. Am. Chem. Soc.*, **63**, 141 (1941)

[221] B. Topley and B. Raistrick, *Thorpe's Dictionary of Applied Chemistry*, Longmans Green, London, 1949, Vol. IX, p. 520

[222] H. S. Booth and G. E. Seegmiller, *Inorganic Syntheses*, ed., W. C. Fernelius, McGraw-Hill Book Co , New York, 1946, Vol. II, pp. 151–52. E. Berger, *Compt. rend.*, **146**, 400 (1908).

[223] For synthesis of $POCl_3$ with radioactive P^{32} see T. Ishiguro, J. Kozatani, and H. Mogi, *J Pharm. Soc , Japan*, **73**, 1140 (1953).

oxide to make POF_3.[224] In addition, phosphorus oxyfluoride has been prepared from phosphorus oxychloride by reacting the latter with such salts as the lead, silver, or zinc fluoride.

The mixed oxyhalides which have been described in the literature are POF_2Cl, $POFCl_2$, POF_2Br, $POFBr_2$, $POCl_2Br$, and $POClBr_2$. The fluorine-containing mixed oxyhalides can be made by treating either phosphoryl trichloride or phosphoryl tribromide with antimony trifluoride.[225] Phosphoryl dichlorobromide, $POCl_2Br$, was first prepared by treating $C_2H_5POCl_2$ with bromine drop-wise, followed by separation of the volatile ethyl bromide through fractional distillation.[226] Phosphoryl chlorodibromide was isolated[227] from the products of the action of dry HBr on $POCl_3$ vapor at 400–500°C.

Electron diffraction studies[182] and microwave spectra[228] have shown that POF_3, $POCl_3$, $POBr_3$, POF_2Cl, and $POFCl_2$ are simple structures in which each phosphorus atom is tetrahedrally surrounded by the four other atoms. Molecular constants obtained from these studies are reported in Table 5-4. It is interesting to note that the P-Cl distance in all of these compounds corresponds to very little π-bonding, whereas the P-F and P-Br atom-center distances indicate that there is approximately 1/3 π-bond per σ-bond. In $POCl_3$, however, the oxygen atom has an unduly large amount of π-bond character—approximately one π-bond per σ-bond—so that the lack of π-character in the P—Cl bond is made up by an accentuation of π-character in the P—O bond. Raman,[128,129,229] ultraviolet,[132] and microwave[134] measurements have been carried out on the phosphorus oxyhalides, and these measurements are found to be in agreement with the structure determined from the electron diffraction studies. Raman spectra[230,231] of the mixed

[224] For example, see G. Montel, *Bull soc chim France*, **1952**, 379. For a related paper, see G. Montel and G. Chaudron, *Compt. rend.*, **233**, 318 (1951).

[225] H. S. Booth and C. G. Seegmiller, *J. Am. Chem. Soc*, **61**, 3120 (1939).

[226] N. Menschutkin, *Liebig's Ann.*, **139**, 345 (1886); *Bull. soc. chim.*, **6**, 481 (1866).

[227] A. Besson, *Compt. rend.*, **122**, 814 (1896). For the simultaneous preparation of all of the mixed phosphoryl chlorobromides by oxygenation of mixtures of PCl_5 and PBr_5, see M. L. Delwaulle and F. François, *Compt. rend.*, **222**, 1173 (1946).

[228] Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952); N. J. Hawkins, V. W. Cohen, and W. S. Koski, *ibid.*, **20**, 528 (1952); W. Gordy, *Ann. N. Y. Acad. Sci.*, **55**, 774 (1952); S. J. Senatore, *Phys. Rev.*, **78**, 293 (1950).

[229] M. L. Delwaulle and F. François, *Bull. soc. chim. France, Mem. 13*, **1946**, 206; H. Gerding and M. van Driel, *Rec. trav. chim.*, **61**, 419 (1942); A. Simon and G. Schulze, *Naturwissenschaften*, **25**, 669 (1937).

[230] M. L. Delwaulle and F. François, *Compt. rend.*, **220**, 817 (1945), *ibid.*, **222**, 550 (1946).

[231] M. L. Delwaulle and F. François, *J. chim. phys.*, **45**, 50 (1948).

phosphorus oxyhalides have been investigated, and Raman studies on mixtures of $POCl_3$ and $POBr_3$ show that at room temperature there is no exchange of halogen atoms to give mixed oxyhalides This should be compared with the more rapid exchange reported by the same workers for the phosphorus trihalides.[123] Early workers[232] determined molecular weights of the oxyhalides by vapor density measurements and found that the densities corresponded to the simple formula POX_3. Phosphorus oxybromide has been used in determining the atomic weight of phosphorus.[233] The resulting atomic weight was 30.975, a value which is in perfect agreement with the presently accepted one.

Pyrophosphoryl chloride, $P_2O_3Cl_4$, has been made and characterized by several investigators. In the most recent study,[234] the original preparation of this material by Geuther and Michaelis was repeated and found to be a very workable method. According to this procedure, phosphorus trichloride is oxidized by nitrogen dioxide to give a yield of approximately 10% of the pyrophosphoryl chloride, which is separated from the other reaction products by distillation. Another even simpler procedure[235] for its preparation is to add water to orthophosphoryl chloride, according to the following simplified equation, and then to distill under vacuum so as to volatilize the hydrogen chloride and fractionate the pyrophosphoryl chloride from other phosphoryl chlorides.

$$2\ POCl_3 + H_2O \longrightarrow Cl_2(O)POP(O)Cl_2 + 2\ HCl \qquad (5\text{-}75)$$

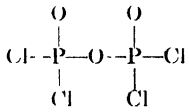
A yield of about 15% based on $POCl_3$ is obtained. Pyrophosphoryl chloride is a colorless, fuming liquid which remains liquid at low temperatures, where orthophosphoryl chloride, $POCl_3$, is a solid. The liquid has a specific gravity of 1.58 and a boiling point of 210–215°C., at which temperature there is some decomposition. Presumably, this is a compound, since it can be distilled without destruction and has a definite boiling point at reduced pressures. Pyrophosphoryl chloride is believed to have the following structure.

[232] T. E. Thorpe and J F. Hambly, *J. Chem. Soc. (London)*, **55**, 759 (1889); *Chem. News*, **60**, 254 (1889) (POF_3); C. A. Wurtz, *Ann. chim. et phys.*, **20**, 472 (1847) ($POCl_3$); J. H. Gladstone, *Phil. Mag.*, **35**, 345 (1849); *J. Chem. Soc. (London)*, **3**, 5 (1851); E. Berger, *Compt rend.*, **146**, 400 (1908), *Bull soc. chim. France*, **3**, 721 (1908) ($POBr_3$).

[233] O. Honigschmidt and F. Hirschbold-Wittner, *Z. anorg. u. allgem. Chem.*, **243**, 355 (1940).

[234] R. Klement and K. H. Wolfe, *Z. anorg. u. allgem. Chem.*, **282**, 149 (1955), A. Geuther and A. Michaelis, *Jena Z.*, **7**, 103 (1871); *Ber.*, **4**, 766 (1871).

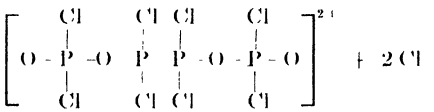
[235] M. Viscontini and K. Ehrhardt, *International Union Pure Applied Chemistry, Colloquium of Section for Inorganic Chemistry, Munster*, Sept., 2–6, 1954, Verlag Chemie, Weinheim, Germany, 1954, p. 232.



(5-76)

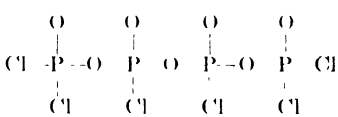
The molecular weight of pyrophosphoryl chloride in camphene was found to correspond to the formula given above

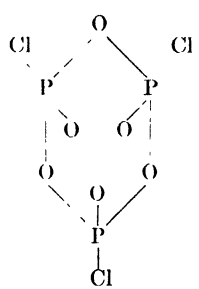
Several other oxyhalides of phosphorus having formulas different than the phosphorus ortho- or pyrophosphoryl halides have occasionally been described. The empirical formulas given in the literature for these compositions are $P_2O_2Cl_5$,[234-236] PO_2Cl,[237,238] $P_7O_{15}Cl_5$,[238] as well as PO_2I_2 and $P_3O_8I_6$.[239] The oxychloride with the empirical formula $P_2O_2Cl_5$ is said[236] to have a double molecular weight and may exhibit the following ionic structure



(5-77)

The other two oxychloride compositions, PO_2Cl and $P_7O_{15}Cl_5$, belong to the family of halides of the condensed phosphoric acids. Structures of typical chain and ring phosphoryl chlorides belonging to this family have been suggested by recent workers[235,240] and are depicted below:





(5-78)

The proposed chain compounds (polyphosphoryl chlorides) have the formula $P_nO_{2n-1}Cl_{n+2}$, and the proposed ring compounds (metaphosphoryl chlorides), $P_nO_{2n}Cl_n$. Because the phosphoryl halides are un-ionized, the random reorganization theory (see pp. 722–744) predicts a large amount of

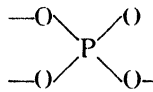
[236] R. Klement, O. Koch, and K. H. Wolfe, *Naturwissenschaften*, **41**, 139 (1954).

[237] G. Gustavson, *Ber.*, **4**, 853 (1871). A. Besson, *Compt. rend.*, **124**, 153, 763, 1099 (1897); *ibid.*, **132**, 1556 (1901).

[238] G. N. Huntly, *J. Chem. Soc.*, **59**, 202 (1891).

[239] S. Burton, *Am. Chem. J.*, **3**, 280 (1881).

[240] H. Roux, E. Thilo, and M. Viscontini, *Helv. Chim. Acta*, **38**, 15 (1955).

branching points, *i.e.*  groups The relative amounts of end, middle, and branching groups as well as the relative amounts of orthophosphoryl halide—are given in Figure 12-2F (p 730) as a function of the Cl/P atom ratio which is denoted by the symbol R in the figure. According to this, the viscous liquid having the empirical composition PO_2Cl[237,238] should exhibit 19% of the total phosphorus as end groups, 27% as middle groups, 43% as branching points, and 11% as orthophosphoryl chloride. These various structural units will be found in a variety of molecular structures, according to the theory given in Chapter 12 for flexible molecules.

It should be noted that any phosphoryl chloride molecule or molecular mixture can formally be considered as combinations of P_2O_5 and $POCl_3$ according to the old Berzelius notation; and, indeed, they can be made from such mixtures, as shown by the following equation for the chain compounds.[238]

$$(n-1)\,P_2O_5 + (n+2)\,POCl_3 \longrightarrow 3\,P_nO_{2n-1}Cl_{n+2} \qquad (5\text{-}79)$$

Following the notation used for the condensed phosphoric acids (Chapters 8 and 12), the condensed phosphorus oxyhalides for which the $POCl_3/P_2O_5$ mole ratio is less than unity would be called ultraphosphoryl halides and must exhibit three-dimensional branched and cross-linked structures.[241] The very viscous composition, $P_7O_{15}Cl_5$, described by Huntly[238] lies in this class since, for it, the $POCl_3/P_2O_5$ mole ratio = 5/8. Presumably, this composition is near an azeotrope in the $POCl_3$-P_2O_5 system. (See p. 774 for a discussion of the H_2O-P_2O_5 system which is believed to be similar.)

Properties and Reactions of the Phosphorus Oxyhalides

The physical properties of most of the orthophosphoryl halides are given in Table 5-1, from which it should be noted that at room temperature POF_3 is a gas, $POCl_3$ is a liquid, and $POBr_3$ is a solid. In Table 5-5 some physical properties[242] of $POCl_3$ in addition to those of Table 5-1 are given On both a commercial and scientific level, the largest application for phosphorus oxychloride probably has been in the phosphorylation[243] of organic compounds such as the alcohols.

[241] J. R. Van Wazer and E. J. Griffith, *J Am. Chem. Soc.*, **77**, 6140 (1955).

[242] In addition, detailed viscosity studies have been reported by G. P. Luchinskii, *Z. anorg. u. allgem. Chem.*, **223**, 210 (1935); *Akad. Nauk S.S.S.R. Otdel. Tekh. Nauk, Inst. Mashinovedeniya Soveschanie Vyazkosti Zhidkost. i Kolloid. Rastvorov*, **1**, 41 (1941)

[243] For example, G M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, Chapt 9, pp 211 77.

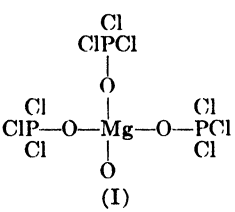
When sufficient amounts of water are used, complete hydrolysis of the phosphorus oxyhalides gives orthophosphoric acid. However, partial hydrolysis leads to intermediate products. In the hydrolysis of phosphorus oxyfluoride, removal of the fluorine atoms occurs[244] through two intermediate steps as indicated below:

$$POF_3 + 3\,H_2O \xrightarrow{(1)} OP(F_2)(OH) + 2\,H_2O + HF \xrightarrow{(2)}$$

$$OP(F)(OH)_2 + H_2O + 2\,HF \xrightarrow{(3)} OP(OH)_3 + 3\,HF \quad (5\text{-}80)$$

If the hydrolysis is carried out in a weakly basic solution, the mono- and difluophosphoric acids can be isolated as salts, of which the nitron salt is the easiest to prepare. Mono- and difluophosphates are reasonably stable in aqueous solution at neutral pH and room temperature. They are discussed in some detail in Chapter 13. Similar halogenated phosphoric acids have not been isolated or characterized as intermediates in the hydrolysis of phosphorus oxyhalides containing halogens other than fluorine. However, such compounds undoubtedly have at least a momentary existence during hydrolysis.

$POCl_3$ is found to react[245] with alkaline earth metal oxides and oxides of similar metals to give compounds such as $CaP_2O_3Cl_6$, $MgP_2O_3Cl_6$, and $MgP_3O_4Cl_9$. The structure of these compounds has never been ascertained. It is possible that they are coordination complexes, as indicated by formula I below, or they may consist of ionic-molecular mixed-crystals, as indicated by formula II; both structural formulas correspond to the empirical crystalline composition, $MgP_3O_4Cl_9$.



(I)

$$Mg^{2+} + 2\,Cl^- + OPCl_3 + Cl_2OPOPOCl_2 \quad (5\text{-}81)$$

(II)

The hydroxides of the alkaline earth metals react similarly to give crystalline products such as $CaH_2P_2O_4Cl_6$. These compounds form adducts with polar organic solvents such as ether, viz. $CaH_2P_2O_4Cl_6 \cdot 2O(C_2H_5)_2$

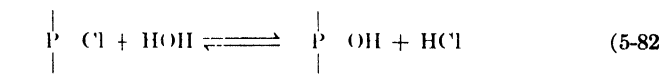
Related to these crystalline compounds are the reaction products between

[244] W. Lange, *Ber.*, **62B**, 786 (1929); *ibid*, **60B**, 962 (1927), W Lange and R Livingston, *J. Am. Chem. Soc.*, **72**, 1280 (1950).

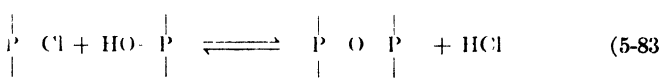
[245] H. Bassett, Jr., and H. S. Taylor, *J Chem. Soc*, **99**, 1402 (1912); M. Garino and M. Raffaghello, *Gazz. chim. ital.*, **54**, 351 (1924).

alkaline earth metal oxides and pyrophosphoryl chloride. These crystalline reaction products are typified by the calcium compound which has the formula $CaP_2O_4Cl_4$. Since chromatographic analysis shows only orthophosphate when this calcium compound is dissolved in water,[246] it is possible that the compound may be the calcium salt of a postulated dichlorophosphoric acid, viz. $Ca^{2+} + 2O_2PCl_2^-$. This compound can be crystallized with two moles of a solvent ketone or ester, and, furthermore, the two molecules of solvate can be changed by simple recrystallization from another solvent. Thus, by recrystallizing from acetone the compound containing ethyl acetate, the acetone compound is obtained, and vice versa.

Upon adding small amounts of water, of the order of magnitude of one mole or less per mole of $POCl_3$, there is an evolution of HCl, which is rapid at first and then slows down. At room temperature and atmospheric pressure, about one mole of HCl is emitted per mole of H_2O. Heating the resulting liquid under reflux results in the evolution of additional HCl. In the case of the liquid made by adding a mole of H_2O to about two moles of $POCl_3$, refluxing leads to a phase separation of the original liquid, which is quite fluid, into a highly viscous phase and a limpid phase. The lower, viscous phase is composed[240,246] primarily of the condensed phosphoric acids (a distribution of both chains and rings), while the upper phase is primarily pure $POCl_3$. The reactions involved in the interaction between $POCl_3$ and H_2O are given below:



(5-82)



(5-83)

It should be noted from these equations that loss of one mole of HCl per mole of H_2O added to a large excess of $POCl_3$ corresponds to the formation of the presently unknown orthochlorophosphoric acids [$Cl_2PO(OH)$ or $ClPO(OH)_2$] or orthophosphoric acid [$OP(OH)_3$]. Essentially no condensation should occur under these circumstances unless an appreciable amount of free H_2O or HCl can exist in the liquid phase. When condensation does occur upon loss of more than one HCl per H_2O, there is a reasonable probability that a given molecule resulting from condensation will exchange all of its chlorine atoms for —OH groups. Such molecules then form a separate dense, viscous, more strongly ionized phase.

[246] J. W. Gryder, unpublished work at the Monsanto Chemical Co.

Addition Compounds of the Phosphorus Oxyhalides

The phosphorus oxyhalides are known to form rather stable addition compounds, similar to those formed by the phosphorus trihalides and the phosphorus pentahalides. In the case of the trihalides, the usual explanation for the stability of the addition compounds is based on donation of the

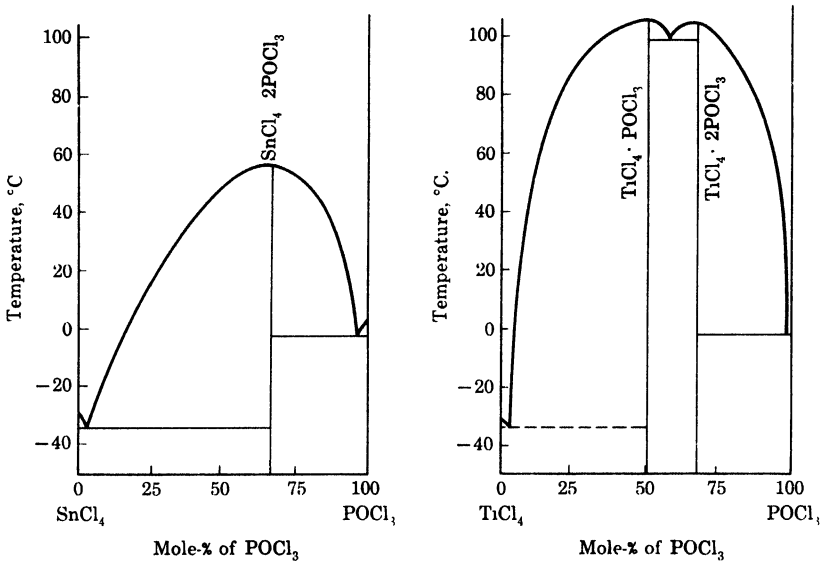


Fig 5-10 Phase diagrams of phosphorus oxychloride with metal halides ($SnCl_4$ and $TiCl_4$)

unshared pair of electrons from the phosphorus to the other element involved in the adduct. On the other hand, the explanation for the addition compounds of the phosphorus pentahalides is that the five halogens are weakly bonded to the phosphorus in order to avoid extensive use of the high energy *d*-orbital. This allows at least one of the halogen atoms to share another pair of its electrons with the electron-acceptor atom in the addition compound. No obvious, simple explanation is available for the formation of addition compounds of the phosphorus oxyhalides, since the phosphorus in this case exhibits hybridization approximating the stable sp^3, and there are no unshared valence-shell electrons Presumably, the addition compounds of the phosphorus oxyhalides take place by either the halogen or oxygen atom acting as an electron donor. However, consideration of the available experimental data does not clearly indicate whether it

is the oxygen or the halogen atom donating electrons or whether in some cases it is one and in other cases the other.

A phase diagram study shows[160] that a 1:1 addition compound is formed between BF_3 and POF_3, although by the same method of measurements there was no evidence of compound formation between BF_3 and PSF_3 or BF_3 and PF_3. $POCl_3$ fails to react with BF_3, but the adduct $POCl_3 \cdot BCl_3$ has been made.[247] The adduct $POCl_3 \cdot BBr_3$ has also been described recently.[248] Other adducts of $POCl_3$ are[206,248] $POCl_3 \cdot AlCl_3$, $POCl_3 \cdot AlBr_3$, $2\ POCl_3\ AlI_3$, $POCl_3 \cdot SbCl_5$, $2\ POCl_3 \cdot TiCl_4$, $POCl_3 \cdot TiCl_4$,[249] $POCl_3\ SnCl_4$, $POCl_3 \cdot TeCl_4$, $POCl_3\ 2\ ZrCl_4$, and $POCl_3 \cdot MoCl_5$. To illustrate the stability of the $POCl_3$ complexes, two phase diagrams between $POCl_3$ and a metal chloride are shown in Figure 5-10. A study based on the use of the parachor indicates that the $POCl_3$ complexes of $SnCl_4$ and of $TiCl_4$ are largely dissociated in the liquid.[250] Through the formation of the addition compound of $POCl_3$ or of the other phosphorus oxyhalides, $ZrCl_4$ can be separated from $HfCl_4$ by fractional distillation.[251] Because of the interest in the separation of hafnium and zirconium in nuclear energy work, these complexes have been the subject of extensive study during the last few years.

Phosphorus oxychloride is a better fire extinguishing chemical than is carbon tetrachloride. This has been attributed to greater polar character in the P—Cl bond than in the C—Cl bond.[252]

Phosphoryl Chloride as a Solvent

In recent years there has been considerable interest in nonprotonic solvents and reactions in such solvents which are at least formally equivalent to acid-base reactions in water. Phosphorus oxychloride is a nonprotonic solvent, and its properties are compared with those of water in Table 5-5 It should be noted that in many respects phosphorus oxychloride is quite similar to water—the boiling points, freezing points, and viscosities are quite close, as are the molar heats of vaporization. Moreover, they both have a low electrical conductivity, which indicates only a small amount of

[247] A B. Burg and M. K. Ross, *J Am. Chem Soc*, **65**, 1637 (1943)

[248] V. Gutmann, *Z. anorg. u. allgem Chem*, **269**, 279 (1952).

[249] W. L. Groeneveld, J W van Spronsen, and H. W. Kouwenhoven, *Rec. trav. chim.*, **72**, 950 (1953)

[250] F. B. Garner and S Sugden, *J. Chem. Soc*, **1929**, 1298.

[251] E. M. Larsen, J. Howatson, A M. Gammill, and L. Wittenberg, *J. Am. Chem. Soc.*, **74**, 3489 (1952), *Technical Report III*, NP-3643 [*Nuclear Sci. Abst.*, **6**, 297 (1952)] Jan. 31, 1951, 13 pp., D M. Gruen and J. J Katz, *J. Am. Chem Soc.*, **71**, 3843 (1949) A. E. van Arkel and J. H. de Boer, *Z. anorg. u. allgem. Chem.*, **141**, 289 (1924).

[252] P. Carré and L. Peigné, *Compt rend.*, **208**, 108 (1939)

ionization. Since it is hard to purify $POCl_3$ from its reaction products with water (phosphoric acid and hydrogen chloride), it is quite possible that the electrical conductivity of absolutely pure $POCl_3$ could be about as low as that of water. The specific conductivity of phosphoryl chloride is found to pass through a maximum at 88°C., while, over the same temperature range, both the density and viscosity decrease monotonically. This has been explained as solvation of the anion,[253] as indicated by equation 5-86 below, decreasing with increasing temperature. In spite of the similarities between H_2O and $POCl_3$, it must be remembered that there is a large amount of hydrogen bonding in pure water and in many aqueous solutions, whereas a similar internal binding mechanism is not readily conceivable for phosphoryl chloride.

TABLE 5-5
Properties of Phosphorus Oxychloride as Compared to Water

	$POCl_3$	H_2O
Molecular weight	153 4	18 02
Melting point	+1 25°C	0 00°C
Boiling point	+105 8°C.	+100 0°C
Critical temperature	329°C	374 0°C
Density at 25°C	1 645 g /cm ^{3}	0 997 g /cm ^{3}
Molecular volume at 25°C	93 3 cm ^{3}	18 07 cm ^{3}
Heat of vaporization	8 06 kcal /mole	9 71 kcal /mole
Trouton's constant	21 3 cal /°K.	26 0 cal /°K
Surface tension at 25°C.	31 6 dynes/cm.	72 0 dynes/cm
Viscosity coefficient at 25°C.	1 065 centipoises	0 896 centipoise
Dielectric constant at 25°C.	13 7	78 54
Measured electrical conductivity at 25°C.	1 6 × 10^{-6} mhos/cm	4 3 × 10^{-8} mhos/cm.
Cryoscopic constant	7 68 deg /mole solute	1 86 deg /mole solute
Ebullioscopic constant	5.47 deg /mole solute	0 52 deg./mole solute

It is interesting to compare the usual solvent, water, with phosphorus oxychloride. Thus, water ionizes as shown in equations 5-84, the second of which emphasizes hydration of the cation. It is believed[254] that $POCl_3$ ionizes as shown in equations 5-85 and 5-86.

[253] V. Gutmann, *Monatsh.*, **83**, 164 (1952), *Z. anorg. u. allgem Chem.*, **269**, 279 (1952); *ibid.*, **270**, 179 (1952). For earlier workers, see G. Oddo and A. M. Mannessier, *Gazz. chim. ital.*, **41**, II, 212 (1912); *Z. anorg. Chem.*, **79**, 281 (1913); P. Walden, *ibid.*, **68**, 307 (1911); *ibid.*, **74**, 310 (1912).

[254] V. Gutmann, *Oesterr. Chem.-Ztg.*, **56**, 126 (1955); V. Gutmann and F. Mairinger, *Z. anorg. u. allgem. Chem.*, **289**, 279 (1957); S. J. Gill, *University of Illinois Inorganic Seminars*, **1952–53**, 12 (1952) (mimeographed).

Water

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{or} \quad 2\,H_2O \rightleftharpoons H_3O^+ + OH^- \tag{5-84}$$

Phosphorus oxychloride

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^- \tag{5-85}$$

or perhaps

$$2\,POCl_3 \rightleftharpoons POCl_2^+ + POCl_4^- \tag{5-86}$$

If we assume[255] that an acid is a dissolved substance which gives the same cation as the cation of the slightly ionized solvent, and that a base is a dissolved substance giving the same anion as the slightly ionized solvent, we can again compare water to phosphorus oxychloride to demonstrate what substances can be defined as acids and what substances as bases in $POCl_3$. The simplest type of acid and base consists of compounds which merely dissociate when put into the solvent. Examples of such "acids" and "bases" are given in equations 5-87 and 5-88. There is another type of acid and base which achieves its functionality by reaction with the solvent to give a substance which then ionizes as an acid or a base. Examples of such an "acid" and "base" are given for water in equation 5-89 and for phosphorus oxychloride in equation 5-90.

In water

$$\text{Acid} \quad CH_3COOH \rightleftharpoons H^+ + CH_3CO_2^- \tag{5-87}$$

$$\text{Base} \quad AgOH \rightleftharpoons Ag^+ + OH^-$$

In phosphorus oxychloride

$$\text{Acid} \quad POCl_2Br \rightleftharpoons POCl_2^+ + Br^-$$

$$\text{Bases} \quad PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$$

$$KCl \rightleftharpoons K^+ + Cl^- \tag{5-88}$$

In water

$$\text{Acid} \quad CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

$$\text{Base} \quad NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{5-89}$$

In phosphorus oxychloride

$$\text{Acid} \quad AlCl_3 + POCl_3 \rightleftharpoons POCl_2^+ + AlCl_4^-$$

$$\text{Base} \quad C_5H_5N + POCl_3 \rightleftharpoons C_5H_5N\,POCl_2^+ + Cl^- \tag{5-90}$$

[255] L. Ebert and N. Konopik, *Oesterr. Chem. Ztg.*, **50**, 184 (1949). For a more general acid-base theory along these lines, see M. Usanovich, *J. Gen. Chem. U.S.S.R.*, **9**, 182 (1939).

Conductivity studies[254] of analog acid-base reactions have been carried out in $POCl_3$, and two typical titration curves are shown in Figure 5-11. The first curve corresponds to the reactions given in equation 5-91 below, where it should be noted that there is a two-step process leading to the formation of a soluble "acid salt" and finally to the precipitation of an insoluble "normal salt." It should be noted that in $POCl_3$ a quaternary ammonium chloride acts as a "base," just as a quaternary ammonium hydroxide acts as a base in H_2O

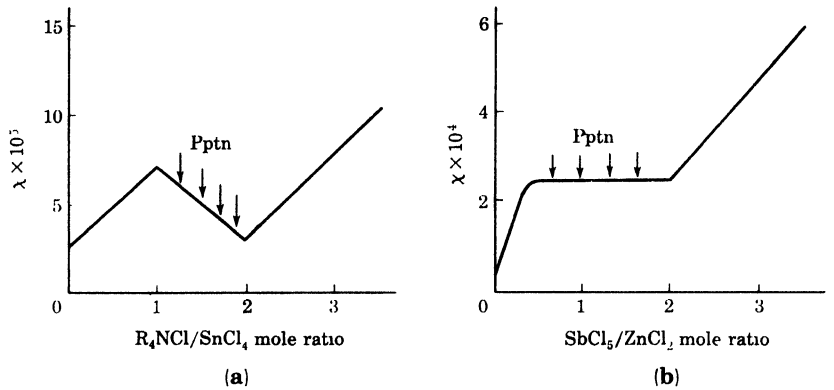


Fig 5-11. Acid-base titrations in $POCl_3$ Graph **(a)** refers to the titration of a $POCl_3$ solution of $SnCl_4$ by a solution of R_4NCl in $POCl_3$ and Graph **(b)** to the titration of a $POCl_3$ solution of $ZnCl_2$ by $SbCl_5$ in $POCl_3$

$$\underset{\text{"acid"}}{(POCl_2)_2^{2+}(SnCl_6)^{2-}} + \underset{\text{"base"}}{(R_4N)^+Cl} \xrightarrow{(1)}$$

$$\underset{\text{soluble "acid salt"}}{(R_4N)^+(POCl_2)^+(SnCl_6)^{2-}} + \underset{\text{solvent}}{POCl_3} \xrightarrow{(2)} \qquad (5\text{-}91)$$

$$\underset{\text{insoluble "normal salt"}}{(R_4N)_2^{2+}(SnCl_6)^{2-}}\downarrow + \underset{\text{solvent}}{2\,POCl_3}$$

The second titration curve shown in Figure 5-11 corresponds to the reaction between the "base," zinc chloride, and the "acid" consisting of the addition compound between phosphorus oxychloride and antimony pentachloride to give the slightly soluble salt zinc hexachloroantimoniate. It should be noted in the titration curve that when the slightly soluble "salt" begins to precipitate, the conductivity remains constant until the precipitation is completed, in the same manner as is found when a slightly soluble salt is

formed by an acid-base reaction in water. The equation for the reaction is given below

$$\underset{\text{"base"}}{Zn^{2+}(Cl_2)^{2}} + 2\,\underset{\text{"acid"}}{(POCl_2)^{+}(SbCl_6)^{-}} \longrightarrow \underset{\substack{\text{slightly soluble "salt"}}}{Zn^{2+}(SbCl_6)_2^{2-}} + 2\,\underset{\text{solvent}}{POCl_3} \quad (5\text{-}92)$$

The purification of phosphoryl chloride for use as a solvent requires the elimination of all traces of water and products from the reaction with water, viz. phosphoric acid and hydrogen chloride. The phosphoric acid and any possible free water can be removed by adding P_2O_5 to the phosphorus oxychloride and distilling $POCl_3$ from the mixture, with fractionation so as to

TABLE 5-6

Solubilities and Conductivities of Various Substances in Phosphorus Oxychloride at 20°C

Substance	Classification	Solubility (g /l.)	Specific conductivity at saturation (10^{-5} mho/cm)	Equivalent conductivity (Λ)
LiCl	Base	0 05	0 66	4 0
NaCl	Base	0 31	3 0	6 4
KCl	Base	0 60	3 4	6 7
NH_4Cl	Base	0 46	3 6	6 9
RbCl	Base	0 87	8 3	14 6
CsCl	Base	1 26	11	16 0
$(CH_3)_4NCl$	Base	2 00	55	37 6
KF	Salt	0 40	2 6	6 4
KBr	Salt	0.51	4 3	14 5
KI	Salt	1 71	12	23 1
KCN	Salt	0 73	3 3	7 2
KCNO	Salt	0 80	3 1	9 0
KCNS	Salt	0 76	2 9	6.6

avoid condensed phosphoryl chlorides such as the pyrophosphoryl chloride.[256] The hydrogen chloride can be eliminated by adding metallic sodium and distilling the resulting mixture at atmospheric pressure—a technique which occasionally results in explosions.[253,257] The solubilities and conductivities of a number of substances dissolved in phosphorus oxychloride are given in Table 5-6.

[256] P. Walden. *Z. physik. Chem* , **43,** 445 (1903)

[257] H. P Cady and R. Taft, *J. Phys. Chem* , **29,** 1057 (1925)

THIOPHOSPHORYL HALIDES

The best known of the compounds containing phosphorus, sulfur, and halogens are the thiophosphoryl halides or phosphorus sulfo- or thiohalides corresponding to the formula PSX_3 These compounds are quite similar to the related phosphorus oxyhalides, POX_3, both in their preparation and properties. The preparation of PSF_3, $PSCl_3$, and $PSBr_3$ has been given in *Inorganic Syntheses*.[258] The two procedures presented there for the preparation of $PSCl_3$ correspond to the reaction between phosphorus pentasulfide and phosphorus pentachloride

$$P_4S_{10} + 6\ PCl_5 \longrightarrow 10\ PSCl_3 \qquad (5\text{-}93)$$

and to the reaction between the $Cl_3P \cdot AlCl_3$ adduct and sulfur

$$2\ PCl_3 + Al_2Cl_6 \longrightarrow 2Cl_3P\ AlCl_3$$

$$Cl_3P \cdot AlCl_3 + S \longrightarrow PSCl_3 + AlCl_3 \qquad (5\text{-}94)$$

Another interesting preparation[259] for thiophosphoryl chloride is shown in the following equation.

$$3\ CCl_4 + P_4S_{10} \xrightarrow{\Delta} 4\ PSCl_3 + 3\ CS_2 \qquad (5\text{-}95)$$

Mixed thiophosphoryl fluorochlorides and fluorobromides can be made[260] by treating $PSCl_3$ or $PSBr_3$ with SbF_3

The molecular structures of $PSBr_3$, $PSFBr_2$, and PSF_2Br were determined by electron diffraction,[261] and the resulting data are presented in Table 5-4 Structural data on $PSBr_3$ were also obtained from an x-ray study.[262] It is interesting to note that the crystal structure of $PSCl_3$ is very similar to that of SnI_4. Raman spectral studies[128,237,263] on various thiophosphoryl halides, as well as a microwave study[228] of PSF_3 are in accord with the x-ray and electron diffraction work, which indicate that the phosphorus is tetrahedrally surrounded by the three chlorine atoms plus the sulfur atom, and that there is only one phosphorus per molecule The infrared spectrum of

[258] H S. Booth and C A Seabright, *Inorganic Syntheses*, McGraw-Hill Book Co., New York, 1946, Vol II, pp 153–54 ($PSBr_3$); T Moeller, H. J Birch, and N. C. Nielsen, *ibid.*, 1953, Vol. IV, pp. 71–3; D. R. Martin and W. M. Duvall, *ibid.*, Vol V, pp. 73–4 ($PSCl_3$).

[259] R de Fazi, *Atti congr naz chim pura ed appl*, II, **1926**, 1293.

[260] H. S. Booth and M. C. Cassidy, *J. Am Chem. Soc*, **62**, 2369 (1940); H. S. Booth and C. A Seabright, *ibid*, **65**, 1834 (1943).

[261] J. H. Secrist and L. O. Brockway, *J. Am Chem. Soc.*, **66**, 1941 (1944).

[262] K. Suenaga, *J. Chem. Soc. Japan*, **62**, 107, 227 (1941); I. Nitta and K. Suenaga, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **31**, 121 (1937).

[263] M. L. Delwaulle and F. François, *Compt. rend*, **226**, 894 (1948); H. Gerding and R. Westrik, *Rec. trav. chim.*, **61**, 842 (1944); V. N. Thatte, *Nature*, **138**, 468 (1936).

thiophosphoryl chloride has also been studied.[264] The physical properties of several thiophosphoryl halides are given in Table 5-1.

A number of compositions having various ratios of phosphorus, sulfur, and halogen other than the 1:1:3 ratio corresponding to the orthothiophosphoryl halides have been reported in the early literature.[265] Chlorides and bromides which have been reported are PS_2Cl_5, PS_5Cl_2, PS_2Br (?), $P_2S_3Br_4$, P_2SBr_6, and $PSBr_2(SH)$. Some of these formulas correspond to amorphous and some to crystalline compositions, and the existence of the crystalline species has not been well established. The phosphorus thioiodides present an even more confused picture. The products reported in the literature correspond to the following empirical compositions: $P_4S_3I_2$, PSI, P_2SI_2, P_2SI_4, and $PS_{24}I_3$ ($2\ PI_3 \cdot 3\ S_8$) A phase diagram of the system PBr_3-$PSBr_3$ showed[266] no evidence of the existence of the previously reported compound P_2SBr_6 ($=PBr_3 \cdot PSBr_3$). Also a reported hydrate of $PSBr_3$ was shown to be merely an impure sample.[266] The whole subject of phosphorus-sulfur-halogen compounds having molecular structures containing more than one phosphorus or more than one sulfur atom should be investigated by modern methods.

PHOSPHORUS HALOGENOIDS

The cyanates, thiocyanates, and cyanides of phosphorus can be considered as halogenoids,[267,268] since the NCO, NCS, and CN groups act very similarly to the halides. The compounds $P(NCO)_3$, $P(NCS)_3$, and $P(CN)_3$ are very similar to the trihalides, whereas the compounds $PO(NCO)_3$ and $PO(NCS)_3$ are similar to the oxyhalides, and $PS(NCO)_3$ resembles the sulfohalides. These halogenoid compounds are prepared by replacing the halogen of PCl_3 with isocyanate, isothiocyanate, and cyanide radicals. Thus, $P(NCO)_3$ is made by reacting PCl_3 with silver isocyanate in benzene, and $P(NCS)_3$ comes from the reaction with $POCl_3$ and AgNCS in xylene. Likewise, $PO(NCO)_3$ is made by combining $POCl_3$ with AgNCO in benzene.

[264] G Cillento, D A. Ramsay, and R. N. Jones, *J. Am Chem Soc.*, **71**, 2753 (1949).

[265] J. W Mellor, *A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1928, Vol. VIII, pp. 1071–80.

[266] A. E. van Arkel and F. J. Lebbink, *Rec. trav. chim.*, **56**, 208 (1937).

[267] H. H. Anderson, *Inter. Union Pure Applied Chem , Colloquium of Section for Inorg. Chem , Munster*, Sept 2–5, 1954, Verlag Chemie, Weinheim, Germany, 1954, p. 235.

[268] H. H. Anderson, *J. Am Chem. Soc.*, **64**, 1757 (1942); G. S. Forbes and H H. Anderson, *ibid.*, **65**, 2271 (1943), *ibid* , **62**, 761 (1940), H. Gall and J. Schüppen, *Ber.*, **63B**, 482 (1930); A. E. Dixon and J. Taylor, *Proc. Chem. Soc.*, **24**, 238 (1909); *J. Chem. Soc.*, **93**, 2148 (1909); P. Miquel, *Ann. chim.*, **11**, 343 (1877), H. Hubner and G. Wehrhane, *Liebig's Ann.*, **128**, 254 (1863).

Another typical preparation consists of reacting $P(NCO)_3$ with sulfur at 140°C. to get $PS(NCO)_3$.

A number of volatile halogenoid-halides of phosphorus have been prepared.[269] These include $PF_2(NCO)$, $PF(NCO)_2$, $PF_2(NCS)$, $PCl_2(NCO)$, $PCl(NCO)_2$, $PCl_2(NCS)$, and $POCl_2(NCS)$. These compounds are made in the same manner that the mixed halides are prepared. Thus, $PCl_2(NCO)$ is made by reacting $Ag(NCO)$ with an excess of PCl_3, and $PF(NCO)_2$ is made by combining $P(NCO)_3$ with SbF_3.

All of the halogenoids and mixed halogenoid-halides of phosphorus (except for $P(CN)_3$) which have been made to date are volatile liquids which can be purified by distillation. The reactions of these compounds are very similar to the halides. For example, they hydrolyze readily in water. From their molar refractivities, it appears that the compounds $P(NCS)_3$ and $PO(NCS)_3$ are both isothiocyanates.[267] However, the "isocyanates" such as $P(NCO)_3$ could actually be cyanates; and nothing is known about the detailed structure of $P(CN)_3$.[270]

TABLE 5-7

Reactions between Halides and Halogenoids Which Can Be Driven to Completion by Volatilization[a] of a Product

$P(NCO)_3 + AlCl_3 \longrightarrow PCl_3 \uparrow + Al(NCO)_3$

$C_6H_5PCl_2 + (C_2H_5)_2Si(NCS)_2 \longrightarrow C_6H_5P(NCS)_2 + (C_2H_5)_2SiCl_2 \uparrow$

$PO(NCS)_3 + n\text{-}C_{12}H_{25}SiCl_3 \longrightarrow POCl_3 \uparrow + n\text{-}C_{12}H_{25}Si(NCS)_3$

$2\ C_6H_5PCl_2 + Ge(NCO)_4 \longrightarrow 2\ C_6H_5P(NCO)_2 + GeCl_4 \uparrow$

$2\ C_6H_5PCl_2 + SiBr_4 \longrightarrow 2\ C_6H_5PBr_2 + SiCl_4 \uparrow$

$3\ C_6H_5PCl_2 + 2\ n\text{-}C_4H_7SiI_3 \longrightarrow 3\ C_6H_5PI_2 + 2\ n\text{-}C_4H_7SiCl_3 \uparrow$

$PO(NCS)_3 + 3\ C_6H_5COCl \longrightarrow POCl_3 \uparrow + 3\ C_6H_5CO(NCS)$

$2\ PBr_3 + 3\ (CH_3)_2Si(HNC_6H_5)_2 \longrightarrow 2\ P(HNC_6H_5)_2 + 3\ (CH_3)_2SiBr_2 \uparrow$

$PBr_3 + 3\ (CH_3)_3Si(OCOCH_2Cl) \longrightarrow P(OCOCH_2Cl)_3 + 3\ (CH_3)_3SiBr \uparrow$

[a] In the reactions above, an arrow (↑) shows the compound which distills from the system

The compounds $P(NCO)_3$, $PS(NCO)_3$, $PO(NCO)_3$, and $P(NCS)_3$ undergo polymerization upon standing to give solid substances of unknown structure. Anderson has suggested that these polymers may be cyanurates or thiocyanurates.[267] It is interesting to note that $PO(NCS)_3$ does not polymerize.

Exchange reactions between the phosphorus halogenoids and the halides of various metals, as well as between the phosphorus halides and the halo-

[269] H. H. Anderson, *J. Am. Chem. Soc.*, **69**, 2495 (1947), *ibid.*, **67**, 2176 (1945).

[270] M. Delépine, *Ann. chim. (Paris)*, **25**, 557 (1912).

genoids of various metals have been studied.[271] Presumably, in the liquid state, an equilibrium is reached. This equilibrium can be driven in one direction by distillation of the most volatile compound from the liquid. A listing of typical reactions illustrating the distillation of a volatile product from the mixture is given in Table 5-7.

ORGANIC DERIVATIVES OF PHOSPHORUS HALIDES

There are three organic derivatives of the phosphorus trihalides: RPX_2, R_2PX, and R_3P. Related to these are the organic derivatives of the halogenoids discussed immediately above. The trisubstituted derivatives are identical to the trisubstituted phosphines and have been reviewed earlier in this chapter. This leaves the compounds RPX_2 and R_2PX, called dihalophosphines and monohalophosphines, respectively.

Kosolapoff[272] reviews thirteen methods for preparing the halophosphines and gives a comprehensive review of the literature on these substances.[273] A typical preparation of an organic dihalophosphine consists of heating[274] phosphorus trichloride with the proper dialkylmercury or diarylmercury compound in a sealed tube for several hours at 180–230°C. The reaction generally proceeds by a combination of the routes shown in the following equations.

$$R_2Hg + PCl_3 \longrightarrow RPCl_2 + RHgCl$$

$$RHgCl + PCl_3 \longrightarrow RPCl_2 + HgCl_2 \qquad (5\text{-}96)$$

Some monochlorophosphines are usually obtained as a byproduct, due to the reaction between the dichlorophosphine and the dialkyl- or diarylmercury. The monohalophosphines have often been prepared by thermal decomposition of the compound R_3PCl_2, with the appropriate R. An equation for the formation[275] of diethyl phosphorus chloride by this procedure is given below.

$$(C_2H_5)_3PO + PCl_5 \longrightarrow (C_2H_5)_3PCl_2 + POCl_3$$

$$(C_2H_5)_3PCl_2 \xrightarrow{\Delta} (C_2H_5)_2PCl + C_2H_5Cl \qquad (5\text{-}97)$$

[271] H. H. Anderson, *J. Am Chem Soc*, **75**, 1576 (1953); *ibid*, **74**, 2371 (1952), *ibid.*, **72**, 2761 (1950).

[272] See Chapt. 3, pp 42-57 of ref. 55.

[273] Also see R. B. Fox and L. B. Lockhart, *Chemistry of Organo-phosphorus Compounds*, Naval Research Lab., Washington, D. C., 1948 (N R.L. Rept. C-3323).

[274] B. Gottlieb, *J. Am. Chem. Soc.*, **54**, 748 (1932); F. Guichard, *Ber.*, **32**, 1572 (1899), A. Michaelis, *ibid.*, **13**, 2174 (1880) ($C_2H_5PCl_2$); *ibid*, **6**, 601, 816 (1873); *Ann.*, **181**, 265 (1876) ($C_6H_5PCl_2$ and $C_6H_5PBr_2$).

[275] V. M. Plets, Thesis, Univ. of Kazan, Russia, 1938.

Halogen exchange reactions between HBr and either the mono- or dichlorophosphines have usually been employed in preparing bromophosphines.[275] Likewise, reaction of the organic chlorophosphine with silver cyanide has been used to form the organic cyanophosphine. The reactions of the halophosphines are generally in accord with their structure. As would be expected, the halogen atoms (especially Cl and Br) are readily hydrolyzed off to give the corresponding acids. The halophosphines also form addition compounds because of their ability to donate an electron pair. An interesting type of organic halophosphine has been described in which the organic radical is a fluorocarbon.[276]

At least on a formal basis, four or five of the halides in the phosphorus pentahalides can be substituted by organic radicals, viz., PX_5, RPX_4, R_2PX_3, R_3PX_2, R_4PX, and R_5P. The compounds R_4PX are quaternary phosphonium halides which have been discussed in an earlier section of this chapter. Likewise, the phosphorus pentahalides, PX_5, have been discussed previously. As far as is known, there is only one example of R_5P, and that is pentaphenylphosphorus.[277] This leaves the compounds RPX_4, R_2PX_3, and R_3PX_2 to be discussed here.[273,278] Nearly all of the compounds having the formulas RPX_4 and R_2PX_3 and a significant proportion of the compounds of the type R_3PX_2 which have been prepared to date have been made by reacting the mono- or dihalophosphines with halogens. Indeed, this reaction has lead to the name "halophosphine halides" for this class of compounds. The reactions are usually carried out by dissolving the organic halophosphine in a suitable solvent, such as carbon tetrachloride or tetrachloroethane, and then adding the halogen, using agitation and cooling. The products are isolated by careful evaporation of the solvent under anhydrous conditions.

$$\begin{aligned} RPX_2 + X_2 &\longrightarrow RPX_4 \\ R_2PX + X_2 &\longrightarrow R_2PX_3 \\ R_3P + X_2 &\longrightarrow R_3PX_2 \end{aligned} \qquad (5\text{-}98)$$

Typical compounds which have been prepared by this reaction are $C_2H_5PCl_4$,[274] $C_6H_5PBr_4$,[279] $(C_6H_5)_2PCl_3$,[280] and $(C_6H_5)_3PCl_2$ as well as $(C_6H_5)_3$-

[276] H. J. Emeléus, *J. Chem. Soc*, **1954**, 2979.

[277] G. Wittig and M. Rieber, *Ann.*, **562**, 177, 187 (1949); G. A. Rasuvaev and N. A. Osanova, *Doklady Akad. Nauk. S.S.S.R.*, **104**, 552, 733 (1955).

[278] For twenty-one preparative procedures and a literature review on organic halophosphine halides and phosphoryl halides, see Chapt. 4, pp. 58–77 of ref. 55.

[279] A. Michaelis and H. Kohler, *Ber.*, **9**, 519, 1053 (1876).

[280] A. Michaelis, *Ber.*, **10**, 627 (1877).

PBr_2.[281] Equations 5-98 also apply to compounds in which the symbol R stands for the aryloxy group. Thus, the following compounds have been prepared:[113,282] $C_6H_5OPCl_4$, $(C_6H_5O)_2PCl_3$, and $(C_6H_5O)_3PCl_2$.

The halophosphine halides which have been investigated are yellowish crystalline solids in the case of the chlorides and reddish crystalline solids in the case of the bromides. It is interesting to note that $C_6H_5PBr_4$ reacts[279] with excess bromine to form the compound $C_6H_5PBr_6$—a reaction which must be classed with the formation of the phosphorus septahalides, PX_7. In general, the organic halophosphine halides exhibit the reactions of the phosphorus pentahalides. Presumably, the halophosphine halides are ionized, with the organic radical being in the cation, *i.e.*, $RPCl_4 = [RPCl_3]^+Cl^-$. However, their structure has not been investigated by any of the standard physical techniques with which such ionization could be demonstrated. The main justification for claiming that these compounds are ionic is that both PCl_5 and PBr_5 are ionized in the solid state, and that the quaternary phosphonium compounds are also ionic compounds.

By substituting organic radicals for halogen atoms in the phosphorus oxyhalides, one obtains the series POX_3, $RPOX_2$, R_2POX, and R_3PO. The phosphorus oxyhalides themselves have been discussed earlier in this chapter, and the phosphine oxides, R_3PO, are described in Chapter 6. This leaves the two intermediate compounds, which are often called alkyl- or arylphosphonyl halides. Thio derivatives of these compounds are also well known. Probably the most convenient laboratory method for the conversion of halophosphine halides to phosphonyl halides consists of dissolving or suspending the halophosphine halide in an inert solvent and bubbling sulfur dioxide into the stirred mixture until the reactions described by the following equations are complete. The reactions proceed at a rapid rate, and the product is easily recovered by distillation.

$$\begin{aligned} RPX_4 + SO_2 &\longrightarrow RPOX_2 + SOX_2 \\ R_2PX_3 + SO_2 &\longrightarrow R_2POX + SOX_2 \end{aligned} \qquad (5\text{-}99)$$

The halophosphines react with sulfur to make the thiophosphonyl derivatives. This reaction is usually carried out in a sealed tube or in a suitable solvent at elevated temperatures.

$$\begin{aligned} RPX_2 + S &\longrightarrow RPSX_2 \\ R_2PX + S &\longrightarrow R_2PSX \end{aligned} \qquad (5\text{-}100)$$

[281] A. Michaelis and H. von Soden, *Ann.*, **229**, 295 (1885); K. A. Jensen, *Z. anorg. Chem.*, **250**, 257 (1943).

[282] L. Anschutz and W. Emery, *Ann.*, **239**, 301 (1887); *ibid.*, **253**, 105 (1889).

The organic derivatives of the phosphorus oxyhalides generally exhibit reactions which are similar to those of the inorganic orthophosphoryl halides. They are hydrolyzed by water to the corresponding acids. This reaction is fairly slow, however, probably because the phosphoryl halides are insoluble in water. It is interesting to note that the triarylmethanephosphonyl dichlorides, $[(C_6H_5)_3C]POCl_2$, yield triarylcarbinols and phosphorous acid on being boiled with water.[283] This means that the P–C bond undergoes scission right along with the P–Cl bonds in this compound. The thiophosphonyl halides are relatively stable to water but are quite readily hydrolyzed by alkaline solutions to the respective acid. Prolonged hydrolysis usually leads to the loss of sulfur from these acids and concomitant formation of hydrogen sulfide

[283] A. E. Arbusov and B. A. Arbusov, *J. Russ. Phys.-Chem. Soc.*, **61**, 217 (1929). A. E. Arbusov and K. B. Nikonorov, *Zhur. Obshchei Khim.*, **17**, 2129 (1947).

CHAPTER 6

Oxides, Sulfides, Nitrides, and Related Compounds of Phosphorus

HISTORY

In 1680 Robert Boyle discovered that white clouds which condense to a voluminous white powder are formed when phosphorus is burned in air or oxygen.[1] This material, which is reasonably pure phosphorus pentoxide, was subsequently called flowers of phosphorus.[2]

In 1777, nearly a century after Boyle's work, le Sage prepared an oxide of phosphorus which contained a considerable amount of what is now known as phosphorus trioxide by passing a very slow current of well-dried air through a tube containing fragments of phosphorus at room temperature.[3] This oxide from slow oxidation was confused by some early workers with flowers of phosphorus; however, Lavoisier early recognized a difference between the oxides formed by slow reaction and by high-temperature combustion and inferred the existence of two different substances.[4] In 1816 Dulong clearly demonstrated that there were two different oxides of phosphorus,[5] just as two oxides of carbon were known. Later workers postulated a number of other oxides, so that there is considerable literature concerned with substances alleged to have the following empirical formulas: P_4O, P_2O, P_2O_3, PO_2, P_2O_5, and P_2O_6. Of these, only three are well established—P_2O_3, PO_2, and P_2O_5—and only P_2O_3 and P_2O_5 have been carefully studied.

Marggraf recognized that sulfur reacted vigorously with elemental phosphorus.[2] Shortly thereafter, various authors claimed chemical in-

[1] R. Boyle, *Phil. Trans*, **13**, 196, 428 (1680).

[2] A. S. Marggraf, *Misc. Berolin*, **6**, 54 (1740); *ibid.*, **7**, 324 (1743); *Chem. Schrift (Berlin)*, **1**, 42 (1762).

[3] B. G. le Sage, *Mém acad.*, **1777**, 321.

[4] A. L. Lavoisier, *Mém. acad.*, **1777**, 65.

[5] P. L. Dulong, *Ann. chim. phys.*, **2**, 141 (1816); *Phil. Mag.*, **48**, 271 (1816); *Mem. d'arcueil*, **3**, 405 (1817).

dividuality for a number of phosphorus-sulfur combinations having the following empirical compositions: P_4S, P_2S, P_4S_3, PS, P_4S_5, P_8S_{11}, P_2S_3, P_3S_5, P_4S_7, PS_2, P_4S_9, P_2S_5, PS_3, and PS_6. Of these alleged compounds, only P_4S_3, P_4S_5, P_4S_7, P_2S_5 and perhaps P_2S_3 are recognized today—primarily through the efforts of Stock and coworkers [6-13]

In the early part of the 19th century, Davy, Rose, and Wöhler and von Liebig prepared[14] substances based on phosphorus and nitrogen, probably primarily phospham, PN_2H, by heating phosphorus pentachloride in ammonia. In the paper by Liebig, a remarkable compound, which was so stable that it could be distilled in steam or boiled in acids or alkalies without appreciable decomposition, was described. This compound, which the discoverer called *chlorphosphorstickstoff*, was first thought to have the empirical formula $P_3N_2Cl_5$. However, later workers showed[15] that the empirical formula was really $PNCl_2$. Elucidation of the structure and properties of the phosphonitrilic chlorides, having the empirical formula, $PNCl_2$, was primarily carried out by Stokes [16,17]

SPECTROSCOPIC MOLECULES

Phosphorus forms diatomic molecules with oxygen, nitrogen, and carbon. These diatomic molecules are unstable under ordinary conditions but have been observed spectrographically in the vapor state.[18] Bands[19]

[6] A. Stock and K. Thiel, *Ber.*, **38**, 2720 (1905).

[7] A. Stock and W. Scharfenberg, *Ber*, **41**, 558 (1908).

[8] A. Stock and H. von Bezold, *Ber*, **41**, 657 (1908).

[9] A. Stock, *Ber.*, **42**, 2062 (1909).

[10] A. Stock, *Ber*, **43**, 150 (1910).

[11] A. Stock, *Ber.*, **43**, 414 (1910).

[12] A. Stock, *Ber.*, **43**, 1223 (1910).

[13] A. Stock and K. Friederici, *Ber*, **46**, 1380 (1913).

[14] H. Davy, *Phil. Trans.*, **100**, 231 (1810); H. Rose, *Ann. Physik*, **24**, 308 (1832), *ibid*, **28**, 529 (1833), *Ann.*, **11**, 133 (1834), F. Wöhler and J. von Liebig, *ibid.*, **11**, 139 (1834).

[15] C. Gerhardt, *Ann. chim. et phys*, **18**, 204 (1846), A. Laurient, *Compt. rend.*, **31**, 356 (1850).

[16] H. N. Stokes, *Am. Chem. J.*, **17**, 275 (1895), *ibid*, **18**, 629, 780 (1896); *ibid.*, **19**, 782 (1897), *ibid.*, **20**, 740 (1898).

[17] H. N. Stokes, *Z. anorg. Chem*, **19**, 42 (1899).

[18] For example, see G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, *Diatomic Molecules*, Prentice-Hall, Inc., New York, 1939, pp. 482–94. Also see H. Sponer, *Molekulspectren*, Julius Springer, Berlin, 1935, Tabellen; W. Jevons, *Band Spectra of Diatomic Molecules*, University Press, Cambridge, England, 1932, pp. 272–90.

[19] R. Ramanadham, G. V. S. R. Rao, and C. R. Sastry, *Indian J. Phys.*, **20**, 161 (1946); R. Ramanadham and G. V. S. R. Rao, *Current Sci. (India)*, **14**, 230 (1945); A. K. S. Gupta, *Proc. Phys. Soc. (London)*, **47**, 247 (1935); H. Lessheim and R. Samuel, *Current Sci. (India)*, **3**, 610 (1935), P. N. Ghosh and A. K. S. Gupta, *Nature*, **131**, 841 (1933); P. N. Ghosh and G. N. Ball, *Z. Physik*, **71**, 362 (1931).

corresponding to the transitions $^2\Sigma \rightarrow {}^2\Pi$ and $^2\Pi \rightarrow {}^2\Pi$ (ground state) have been carefully studied in the case of the PO molecule. The excitation energy for this molecule is 143 kcal./mole, and the products of dissociation are a normal oxygen atom and an excited phosphorus atom. The P-O distance in the PO molecule is equal to 1.447 A.

The PN molecule has also been carefully studied.[20] The observed spectral lines for PN correspond to a $\Pi \rightarrow \Sigma$ transition. For this molecule the dissociation energy[21] is 164 kcal /mole and the P-N distance equals 1.491 A. At 900°C., the equilibrium constant,[21] K_{atm}, corresponding to the following dissociation equation, is 100; and at 2000°C., it is 5. The heat of this reaction is −14 2 kcal /mole.

$$2\,PN(g) = P_2(g) + N_2(g) \qquad (6\text{-}1)$$

Thus at 900°C., there is about 2% of PN in an equimolar mixture of nitrogen and phosphorus vapor at a total pressure of 1 atm.

The band systems observed for the PC molecule correspond to $^2\Sigma \rightarrow {}^2\Sigma$ (ground state) and $^2\Sigma \rightarrow {}^2\Pi$ transitions From this spectrum,[22] a dissociation energy of 159 kcal./mole and a P—C bond distance of 1.5622 A. have been calculated.

The diatomic molecules discussed here have been considered in various correlations and theoretical discussions concerned with diatomic molecules and their properties [23]

PHOSPHORUS OXIDES

Preparation and Forms of Phosphorus Pentoxide

Phosphorus pentoxide, which is also commonly known as phosphoric anhydride and phosphoric oxide, is simply called a pentoxide rather than diphosphorus pentoxide since it was found and well described during the early days of chemistry before the Avogadro hypothesis was accepted.

[20] J. Curry, L. Herzberg, and G. Herzberg, *Z. Physik*, **86**, 348 (1933); W. Jevons, *Nature*, **133**, 619 (1934); P. N. Ghosh and A C. Datta, *Z. Physik*, **87**, 500 (1933); J. Curry, L. Herzberg, and G. Herzberg, *J. Chem. Phys*, **1**, 749 (1933), C. H. D. Clark, *Nature*, **135**, 544 (1935).

[21] E. O. Huffman, G. Tarbutton, K. L. Elmore, W. E. Cate, H. K. Walters, and G. V Elmore, *J. Am. Chem. Soc*, **76**, 6239 (1954).

[22] H. Barwald, G. Herzberg, and L. Herzberg, *Ann. Physik*, **20**, 569 (1934).

[23] H. O. Pritchard and H. A Skinner, *J. Chem. Soc.*, **1951**, 945; M. A. Cook, *J. Phys. & Colloid Chem.*, **51**, 407 (1947); K. M. Guggenheimer, *Proc. Phys Soc. (London)*, **58**, 456 (1946); R. F. Barrow and W. Jevons, *ibid*, **56**, 204 (1944), J. W. Linnett, *Quart. Revs. (London)*, **1**, No. 1, 73 (1947); *Trans. Faraday Soc.*, **38**, 1 (1942).

In those times water was written as HO and phosphorus pentoxide as PO_5. Phosphorus pentoxide is a common chemical of commerce which is always made by burning elemental phosphorus in predried air. The usual phosphorus pentoxide of commerce assays 99.5% P_2O_5 or better, with the major impurity being H_2O, present in the form of condensed phosphoric acids from moisture primarily picked up in storage. Lower oxides are found to be present in commercial phosphorus pentoxide in very small amounts—less than 0.01% as P_2O_3. By careful control of the burning operation, it is possible to make phosphorus pentoxide so free of the lower oxides of phosphorus that it will not decolorize dilute, very pale permanganate solutions, even after standing for many hours.

In the usual commercial operation, phosphorus is burned with an excess of dry air and is precipitated from the vapor by cooling in a large chamber. The reaction between phosphorus and oxygen to give phosphorus pentoxide proceeds by a chain mechanism, as described on pages 97–99 and 109–112.

Although reactions have been described at different times in the literature as producing phosphorus pentoxide, it is found in most cases that the substance really obtained is some kind of a condensed phosphate—often an ultraphosphoric acid. In the relatively recent literature, it is said that electrolysis of fused sodium metaphosphate produces P_2O_5 at the anode.[24] Also, it has been claimed that gaseous SO_3 will displace P_2O_5 as such from anhydrous potassium pyrophosphate and potassium metaphosphate (Kurrol's salt).[25] These reactions should be reinvestigated to determine carefully whether anhydrous phosphorus pentoxide was truly produced, since it would be interesting to have a verified reaction other than oxidation of elemental phosphorus for its formation.

The usual purification of phosphorus pentoxide is carried out by sublimation.[26] This technique is quite effective, since azeotropic phosphoric acid[27] (containing 92.4% P_2O_5) has a boiling point of 864°C. at a pressure of 760 mm. of Hg as compared to the subliming temperature of 360°C. for the P_4O_{10} molecule at the same pressure. Some of the earlier workers treated phosphorus pentoxide with ozone to remove lower oxides of phosphorus;[28] however, this step is usually not necessary today.

[24] M. Tzentnershver and J. Szper, *Bull. intern. acad. polonaise sci.*, **1931A**, 364.

[25] P. Baumgarten and C. Brandenburg, *Ber.*, **72B**, 555 (1939).

[26] H. Whitaker, *J. Chem. Soc.*, **127**, 2219 (1925); G. I. Finch and R. H. K. Peto, *ibid.*, **121**, 692 (1922); G. I. Finch and R. P. Fraser, *ibid.*, **129**, 117 (1926); J. Pitha, *J. Chem. Educ.*, **23**, 403 (1946).

[27] G. Tarbutton and M. E. Demming, *J. Am. Chem. Soc.*, **72**, 2086 (1950).

[28] J. J. Manley, *J. Chem. Soc.*, **121**, 331 (1922); L. I. Smith, *J. Am. Chem. Soc.*, **47**, 1850 (1925).

Commercial phosphorus pentoxide, which is condensed from the vapor, is commonly present as the hexagonal, crystalline modification, although there are sometimes various proportions of a powdery amorphous form. By resublimation in a vacuum, it is possible to obtain the hexagonal form (commonly called the H-form) as microscopically observable hexagonal plates. The powdery amorphous form—called the β-form by Yost and Russell[29]—can be obtained pure but usually occurs admixed with the H-form. It is formed by rapid cooling or by other techniques. In addition, there is a stable, orthorhombic modification and another metastable one. The stable modification, called the O′-form, can be made by heating the H-form in a closed system for 24 hr. at 450°C. It consists of horny aggregates of relatively large crystals possessing good cleavage. The metastable orthorhombic modification, called the O-form, is prepared by heating the H-form in a closed system for 2 hr. at 400°C. The product obtained in this way is a chalky aggregate of small orthorhombic crystals. When molten phosphorus pentoxide is cooled with reasonable rapidity, a vitreous form results.

In addition to the three crystalline forms and the two amorphous solids, (powdery and vitreous), there also appear to be two liquid forms of phosphorus pentoxide. When the hexagonal form is melted, an unstable, limpid liquid of high vapor pressure results. Likewise, when the O′ or O-forms are melted, another more viscous liquid of lower vapor pressure is formed. The known glassy modification of P_2O_5 comes from rapid cooling of this latter liquid. The glass corresponding to the less viscous liquid has not yet been prepared. It may be the same as the β-form.

Obviously, the existence of at least four or five solid modifications and two liquid modifications of P_2O_5 was most confusing to early workers. However, during the decade from 1933 to 1943, a series of papers appeared which clarified the question of the complexity of phosphorus pentoxide.[30-32] Of particular note is the work of Smits *et al.*[31] and the truly illuminating

[29] D. M. Yost and H. Russell, *Systematic Inorganic Chemistry*, Prentice-Hall, Inc., New York, 1944.

[30] A. N. Campbell and A. J. R. Campbell, *Trans. Faraday Soc.*, **31**, 1567 (1935); K. Boratynski and A. Nowakowski, *Compt. rend.*, **194**, 89 (1932); *ibid.*, **196**, 691 (1933). A. Nowakowski, *Roczniki Chem.*, **13**, 346 (1933).

[31] A. Smits, E. P. S. Parve, P. G. Meerman, and H. C. J. de Decker, *Z. physik Chem.*, **B46**, 43 (1940); A. Smits, J. A. A. Ketelaar, and J. L. Meijering, *ibid.*, **B41**, 87 (1938); A. Smits, *ibid.*, **A149**, 337 (1930), A. Smits and H. W. Deinum, *Proc. Acad. Sci. Amsterdam*, **33**, 619 (1930); A. Smits and A. J. Rutgers, *J. Chem. Soc.*, **125**, 2573 (1924).

[32] W. L. Hill, G. T. Faust, and S. B. Hendricks, *J. Am. Chem. Soc.*, **65**, 794 (1943).

paper by Hill, Faust, and Hendricks.[32] A brief, up-to-date review has been given by Farr.[33]

Molecular Structures of Phosphorus Pentoxide

Electron diffraction studies[34,35] show that phosphorus pentoxide in the vapor state consists of P_4O_{10} molecules, the structural arrangement of which is shown in Figure 6-1. According to this structure, phosphorus pentoxide vapor consists of molecules having a T_d symmetry with 14

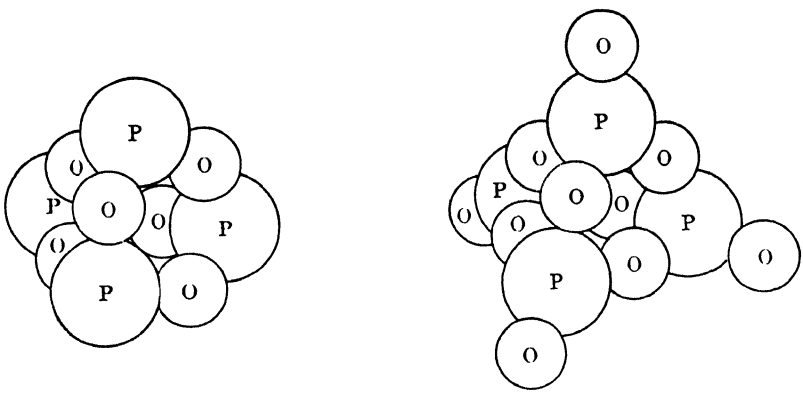


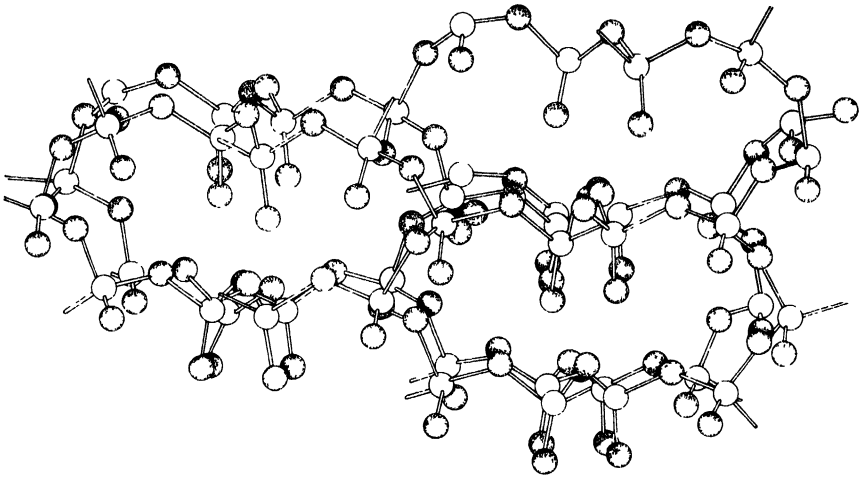
Fig. 6-1. The structures of P_4O_6 and P_4O_{10} as determined from diffraction data and bond theory.

atoms in the molecule. There are two different P-O distances in this molecule. The distance[34] between a phosphorus and any one of its shared oxygen atoms is 1.62 ± 0.02A., whereas, the distance between a phosphorus and its unshared oxygen is 1.39 ± 0.02A. The P—O—P bond angles are 123.5° and the O—P—O angles are 101.5° and 116.5°, with the smaller value referring to the angle between any two of the three oxygen atoms shared by each phosphorus with other phosphorus atoms. The long distance between a phosphorus and a shared oxygen corresponds to essentially no π-bonding, but the short distance between a phosphorus and its unshared oxygen can be attributed to about 1.5–2.0 π-bonds in addition to the σ-bond.

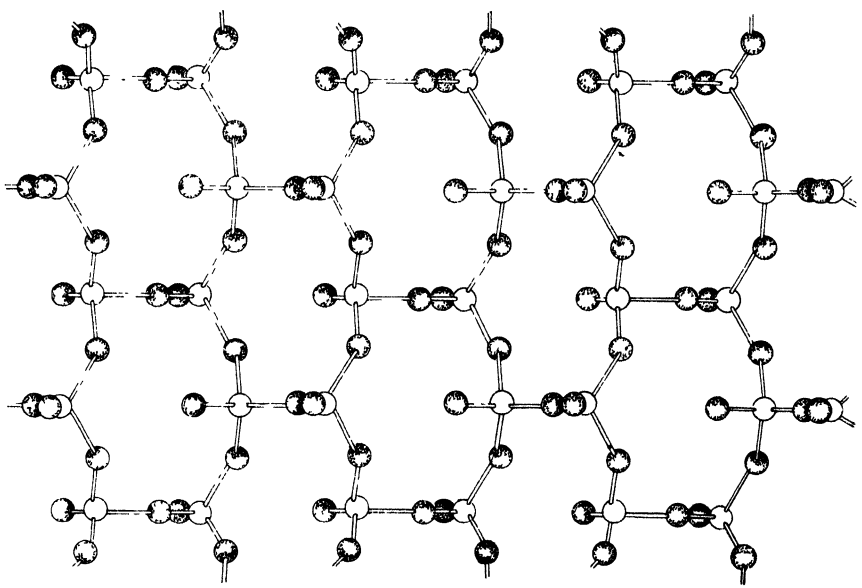
[33] T. D. Farr, *Phosphorus, Properties of the Element and Some of Its Compounds*, Tenn. Valley Author., Wilson Dam, Ala., 1950 (Chem. Eng. Rept. No. 8).

[34] G. C. Hampson and A. J. Stosick, *J. Am. Chem. Soc.*, **60**, 1814 (1938).

[35] L. R. Maxwell, S. B. Hendricks, and L. S. Deming, *J. Chem. Phys.*, **5**, 626 (1937).



The O-form



The O′-form

Fig. 6-2. Structures of the two orthorhombic forms of phosphorus pentoxide. The white balls represent phosphorus atoms and the shaded balls, oxygen atoms.

An x-ray diffraction study of the H-form shows that it consists of P_4O_{10} molecules having the same form and dimensions as were found for this molecule in the vapor state.[36] Raman spectral measurements on the solid H-form are in agreement with this structure.[37] Presumably, the limpid liquid first observed after melting the H-form also consists predominantly of P_4O_{10} molecules.

The O-form of phosphorus pentoxide consists of an infinite sheet polymer.[32,38] In Figure 6-2 a view of the structure of this polymer is shown in the direction of the [011] axis. The isolated oxygen atoms in the structure are all directed upwards so that the *c*-axis of the orthorhombic crystal has polar characteristics. The large rings containing ten phosphorus and ten oxygen atoms should be noted in Figure 6-2. The electron density data for this crystal indicate that the phosphorus and oxygen atoms share electrons and are not ionized.

The O′-form of phosphorus pentoxide[39] is also an infinite sheet polymer, except that in this case the structure consists of corrugated sheets parallel to [100] as shown in Figure 6-2. The interlocking rings in this modification are made up of six phosphorus and six oxygen atoms. Presumably, the vitreous form of P_2O_5 is a three-dimensional network very similar to that described by Zachariasen[40] so that it is made up of various sized rings of alternate phosphorus and oxygen atoms. The structure of glassy P_2O_5 is the subject of a theoretical discussion on pages 719–744. It should be noted that in all of the structures of phosphorus pentoxide, a given phosphorus atom is tetrahedrally surrounded by four oxygen atoms with three oxygens being shared with adjacent PO_4 tetrahedra, each oxygen with a different tetrahedron.

Physical and Chemical Properties of Phosphorus Pentoxide

Density determinations[41] on the vapor of P_4O_{10} correspond to molecular weights of 302 ± 2 in the temperature range of 700–1400°C. as compared

[36] H. C. J. de Decker and C. H. MacGillavry, *Rec. trav. chim.*, **60**, 153 (1941).

[37] H. Gerding and H. C. J. de Decker, *Rec. trav. chim.*, **64**, 191 (1945); H. van Brederode and H. Gerding, *ibid*, **67**, 677 (1948).

[38] H. C. J. de Decker, *Rec. trav. chim.*, **60**, 413 (1941).

[39] C. H. MacGillavry, H. C. J. de Decker, and L. M. Nijland, *Nature*, **164**, 448 (1949).

[40] W. H. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932); *J. Chem. Phys.*, **3**, 162 (1935).

[41] E. V. Britske and E. Hoffmann, *Monatsh.*, **71**, 317 (1938), *Sitzber Akad. Wiss Wien, Math. Naturw. Klasse, ABT*, **11b**, 146, 763 (1938), C. A. West, *J Chem Soc*, **81**, 923 (1902); W. A. Tilden and R. E. Barnett, *ibid*, **69**, 154 (1896).

to the formula weight of 284. This may be due to some association of the P_4O_{10} molecules but is more likely attributable to the presence of a small proportion of high molecular weight ultraphosphoric acids mixed in with the phosphorus pentoxide. However, it should be noted that the apparent association may possibly be an artifact attributable to gas imperfections of the complicated molecule and experimental difficulties. A

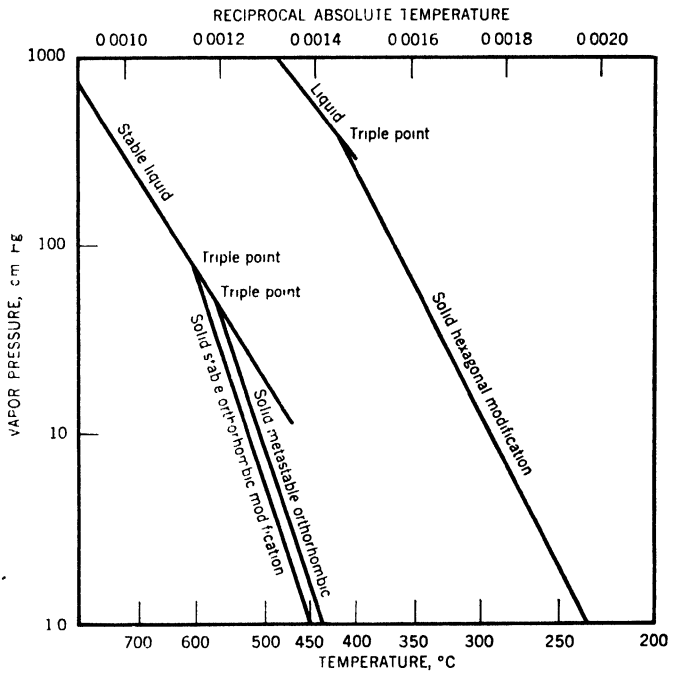


Fig. 6-3 Vapor pressure of the three crystalline and two liquid forms of phosphorus pentoxide

number of measurements have been carried out on the vapor pressure of the various forms of phosphorus pentoxide.[33] The results are shown in Figure 6-3. The conclusion that the O′-form is the most stable solid is in accord with the data shown in Figure 6-3. The triple point, where the solid, its corresponding liquid, and the vapor are in equilibrium, is 420°C. for the H-form. The vapor pressure corresponding to this triple point is 3600 mm. of Hg. For the O-form, the triple-point temperature is 562°C., and the triple-point pressure is 437 mm. of Hg, whereas for the

TABLE 6-1
Physical Properties of Phosphorus Oxides and Sulfides

Formula	Boiling point (°C.)	Heat of vaporization (kcal / mole)	Constants in vapor pressure equations[a]				Melting point (°C)	Heat of fusion[d] (kcal. / mole)	Heat of sublimation[d] (kcal / mole)
			A_{solid}	B_{solid}	A_{liq}	B_{liq}			
P_4O_{10}[H-form]	(340) 360[b]	16 2	4963	9 7163	3542	7 6663	420	6 5	22 7
$(P_2O_5)_n$[O-form]	(605)	(18 7)	7958	11 1698			562	(7 7)	36 4
$(P_2O_5)_n$[O'-form]	(605)	18 7	7411 5	10 4314	4088	6 5359	580	5 2	33 9
$(PO_2)_n$	—	—	—	—	—	—	Sublimes	—	—
P_4O_6	175 4	—	—	—	—	—	23 8	—	—
$P_4O_6S_4$	295	—	—	—	—	—	102	—	—
P_4S_{10}	514 ± 1	—	—	—	—	—	288 ± 2	—	—
P_4S_7	523	—	—	—	—	—	308 ± 3	—	—
P_4S_5	—	—	—	—	4940	8 17	170[c]	—	—
P_4S_3	408	—	—	—	—	—	174	—	—

[a] Log $p_{cm.} = -A/T + B$.
[b] Sublimation temperature.
[c] Probably incongruent, see Figure 6-6.
[d] In terms of the P_4O_{10} molecule of the vapor.

O′-form the triple-point temperature is 580°C., and the corresponding pressure is 555 mm. of Hg.[34]

The physical properties of the various crystalline forms of phosphorus pentoxide are presented in Table 6-1. When heated in an autoclave to elevated temperatures below its melting point, the H-form first transforms into the O-form, which then more slowly transforms into the O′-form, as would be expected from the relative stabilities. At its melting point of 421°C., the H-form produces the liquid of high vapor pressure which then

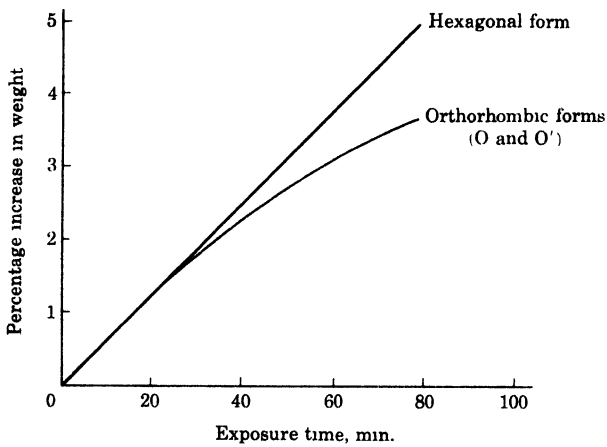


Fig. 6-4 Rate of pick-up of water from air for equal small samples of P_2O_5 spread out in similar dishes.

rather rapidly converts into a glass in which are imbedded crystals of the O-form. At its melting point of 562°C., the O-form transforms to a liquid so viscous that it can almost be called a glass. Apparently the O′-form transforms to the viscous liquid corresponding to this glass at the observed melting point of 580°C. The liquid obtained from the O′-form at its melting point is so viscous that it does not readily assume the shape of its container. Although it is commonly believed that solids never superheat on melting, the O′-form of phosphorus pentoxide can be superheated by as much as 10°C. over its melting point. In this respect it is similar to some silicates[42] and certain organic polymers. Superheating of the solid on melting is probably due to the fact that such melting involves a considerable reorganization of a polymeric structure. Presumably, the infinite

[42] A. L. Day and E. T. Allen, *The Isomorphism and Thermal Properties of Feldspars*, Carnegie Institute, Washington, 1905 (Carnegie Inst. Pub. No. 31), p. 45 *et seq*

sheet polymer corresponding to the O′-form undergoes considerable depolymerization upon melting even though the liquid appears to have a relatively high degree of polymerization itself, based on viscosity.

The H-form of phosphorus pentoxide dissolves extremely rapidly in water, with a hissing sound and the evolution of much heat. The O′-form also gives off considerable heat upon being mixed with water, although it dissolves much more slowly than the H-form. When a limited amount of water is used, the O′-form produces a stiff gel. The slowest of the crystalline forms of P_2O_5 to dissolve is the O-form. Dissolution in this case proceeds by fragmentation of the crystals until a suspension of finely divided particles results. Even in water at 90°C., the O-form of phosphorus pentoxide dissolves slowly. In Figure 6-4 the rate of moisture pick-up is shown for samples of the three crystalline varieties of P_2O_5 exposed to moist air under similar conditions. It should be noted that, although all three varieties appear to absorb moisture at about the same rate initially, the rate of moisture pick-up for the O- and O′-form decreases with time, whereas it continues unabated for the H-form.

Colloidal sols of commercial P_2O_5 in nitrobenzene containing alcohols, phenols, or organic acids have been prepared.[43] Presumably, the reaction of the P_2O_5 with the alcohol, phenol, or acid coats the surface of the particles with a self-generated dispersing agent. Aerosols based on the H-form of P_2O_5 have also been studied.[44]

Chemical Reactions of Phosphorus Pentoxide

Perhaps the most important reaction of phosphorus pentoxide is its ability to take up water. Commercial phosphorus pentoxide is one of the most effective of all drying agents, at least at temperatures below, say, 100°C.[45] When employed as a desiccant, phosphorus pentoxide soon becomes covered with a film of phosphoric acids which can completely seal off the unreacted P_4O_{10} and will continue to absorb moisture until the resulting mixture of phosphoric acids exhibits an appreciable partial pressure of water. This problem, of course, can be remedied easily by properly distributing the phosphorus pentoxide—as on glass wool.

The products formed by dissolving the various varieties of phosphorus pentoxide in water have long been a problem of considerable interest.

[43] F. S. Brown and C. R. Bury, *J. Phys. Chem.*, **29**, 1312 (1925).
[44] T. Tachibana, *J. Chem. Soc. Japan*, **65**, 444 (1944).
[45] D. A. Lacoss and A. W. C. Menzies, *J. Am. Chem. Soc.*, **59**, 2471 (1937).

Investigation by the early authors[46] was carried out either with presently unacceptable analytical techniques giving results in terms of hypothetical ortho-, pyro-, and metaphosphate mixtures or by physical procedures such as conductivity which could not readily be interpreted in terms of the chemistry of the products formed. In the last decade it has been shown[47,48] that the major product (up to 80% of the total P_2O_5) obtained from the careful dissolution of the H-form of phosphorus pentoxide in ice-cold water is the ring compound, tetrametaphosphoric acid. The best study along these lines was based on the use of paper chromatography,[48] which showed 77% of the total P_2O_5 going into tetrametaphosphoric acid, 15% going into tripolyphosphoric acid, with the remaining 8% being rather evenly divided between trimetaphosphoric acid, tetrapolyphosphoric acid, and orthophosphoric acid. This work is discussed in considerable detail on pages 693-696. When the two orthorhombic forms of P_2O_5 were studied, it was found that a considerable proportion of the phosphorus in the hydrolysis products was contained in high molecular weight structures which did not move from the origin in the paper chromatogram.[48] The hydrolysis products and kinetics of the hydrolysis process should be investigated for all of the forms of phosphorus pentoxide, using modern analytical techniques such as paper chromatography, solubility fractionation, and nuclear magnetic resonance measurements.

In addition to its ability to react with free water, phosphorus pentoxide is also very effective in removing water of composition from many organic and inorganic compounds. Thus, water can be taken from anhydrous nitric[49] and sulfuric[50] acids to give nitrogen pentoxide and sulfur trioxide. Likewise, organic amides can be dehydrated to nitriles[51] and methylarylcarbinols can be dehydrated[51] to the respective styrenes by phosphorus pentoxide.

Phosphorus pentoxide reacts very readily with ammonia, either wet or

[46] e.g., S. Ghixelli and K. Boratynski, *Z. anorg. u. allgem. Chem.*, **235**, 225 (1938); A. Travers and Y. K. Chu, *Compt. rend.*, **198**, 2169 (1934), M. A. Rakuzin and A. A. Arseniev, *Chem.-Ztg.*, **47**, 195 (1923), D. Balareff, *Z. anorg. Chem.*, **69**, 215 (1911).

[47] B. Raistrick, *Discussions Faraday Soc.*, **5**, 234 (1949), R. N. Bell, L. F. Audrieth, and O. F. Hill, *Ind. Eng. Chem.*, **44**, 570 (1952). Also see N. I. Rodionova and Ya. V. Khodakov, *J. Gen. Chem. U.S.S.R.*, **20**, 1401 (1950).

[48] E. Thilo and W. Wieker, *Z. anorg. u. allgem. Chem.*, **277**, 27 (1954).

[49] For example, R. Weber, *Ann. Physik*, **147**, 113 (1872), *J. prakt. Chem.*, **6**, 342 (1873).

[50] For example, C. Barreswil, *Compt. rend.*, **25**, 30 (1847), H. S. Evans, *Pharm. J.*, **8**, 127 (1849).

[51] R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley & Sons, Inc., N. Y., 1953, pp. 33, 596.

dry.[52] The products obtained from this reaction are ammonium salts of the condensed phosphates with some P—NH—P linkages, there being, on the average, a number of phosphorus atoms per molecule-ion. The reaction products are dry, amorphous solids and undoubtedly consist of mixtures. They are described in greater detail in Chapter 13. In contact with dry nitrogen tetroxide, phosphorus pentoxide forms[53] a glassy white solid with the empirical formula $P_2O_5 \cdot 2NO$. This product can also be made by direct union of NO and P_2O_5.

Commercial phosphorus pentoxide reacts quite rapidly with alcohols to give organic phosphates, with the exact composition of the product depending on the ratio of the alcohol to P_2O_5.[54] By this reaction it is possible to make esters of the condensed phosphoric acids as well as acid and neutral esters of orthophosphoric acid. In the reaction of phosphorus pentoxide with ethers, esters of various condensed phosphates are formed. Although the reaction with ethers has been studied quite recently,[55] it is still not well understood. At least nuclear magnetic resonance work[56] indicates that the structure presented by Thilo *et al.*[55] is incorrect. Presumably, a random-reorganization mixture of condensed phosphates (see Chap. 13) is obtained from this reaction. Generally speaking, phosphorus pentoxide is found to react with the majority of oxygen-containing organic compounds. Naturally, all of the organic compounds with basic properties, such as amine,[57] readily react with phosphorus pentoxide. As the most condensed member of the series of phosphates (see Chapt. 8), phosphorus pentoxide also will react with the various organic or inorganic phosphates to give products more condensed than the starting phosphates.

An interesting reaction of phosphorus pentoxide occurs with various halides,[58,59] such as calcium fluoride and hydrochloric acid, to form the

[52] H. Fischer, *Über Reactionsprodukte aus Phosphorpentoxyd und Ammoniak und deren Eignung zur Wasserenthartnung*, Dittert, Dresden, 1941. A. Sanfourché, A. Hernette, and M. Fau, *Bull. soc. chim. France*, **47**, No. 4, 273 (1930); E. Moles and J. Sancho, *Anales soc. espan. fis. quim.*, **31**, 172 (1933); *ibid.*, **30**, 701 (1932); L. Harris and C. B. Wooster, *J. Am. Chem. Soc.*, **51**, 2121 (1929).

[53] E. M. Stoddard, *J. Chem. Soc.*, **1945**, 448; *ibid.*, **1938**, 1459.

[54] For example, E. Cherbuliez and H. Weniger, *Helv. Chim. Acta*, **28**, 1584 (1945).

[55] E. Thilo and H. Woggon, *Z. anorg. u. allgem. Chem.*, **277**, 17 (1954); R. Ratz and E. Thilo, *Ann.*, **572**, 177 (1951), also see K. Langheld, *Ber.*, **43**, 1857 (1910); *ibid.*, **44**, 2076 (1911); *ibid.*, **45**, 3737, 3760 (1912).

[56] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

[57] A. C. Buck and H. P. Lankelma, *J. Am. Chem. Soc.*, **70**, 2398 (1948).

[58] G. Montel, *Bull. soc. chim. France*, **1952**, 379; J. M. A. Hoeflake, *Rec. trav. chim.*, **48**, 973 (1929); H. J. Lucas and F. J. Ewing, *J. Am. Chem. Soc.*, **49**, 1270 (1927).

[59] G. Tarbutton, E. P. Egan, Jr., and S. G. Frary, *J. Am. Chem. Soc.*, **63**, 1782 (1941).

phosphoryl halides and some phosphorus tri- and or pentahalides Thus, when calcium fluoride, sodium chloride, and phosphorus pentoxide are heated to 350°C. or above, a mixture of PF_5, POF_3, POF_2Cl, $POFCl_2$, and $POCl_3$ is formed [59]

Phosphorus pentoxide reacts with all basic oxides to give various phosphates In most cases, mixing of the dry oxides at room temperature does not lead to interaction; but, upon heating, the reaction takes place rapidly with the evolution of a considerable amount of heat so that it is autocatalytic. Similar reactions also occur with various salts, such as sodium carbonate or even sodium sulfate, to give the appropriate metal phosphates plus such acid anhydrides as carbon dioxide or sulfur trioxide Examples of this type of reaction are seen in the interaction between phosphorus pentoxide and lime and between phosphorus pentoxide and sodium carbonate In the first case, it is found that when an approximately equimolar mixture of anhydrous lime and commercial phosphorus pentoxide is allowed to stand, nothing happens However, if a few drops of water are sprinkled on this mixture the reaction is then triggered by the evolution of heat from hydration of the phosphorus pentoxide and lime, so that (1) flames are emitted when a large volume of the reaction mixture is used, (2) part of the phosphorus pentoxide is volatilized, and (3) the entire reaction is completed almost instantaneously Likewise, a large volume of a mixture of, say, one or two moles of sodium carbonate per mole of phosphorus pentoxide can be set off by heating a very small section of the mass with a torch Once the reaction is initiated, it rapidly spreads throughout the entire volume of the mixture, which becomes so hot that part of the phosphorus pentoxide is volatilized.

Phosphorus Tetroxide

Although the oxide with the empirical formula PO_2 might better be called phosphorus dioxide or diphosphorus tetroxide, it is commonly known as phosphorus tetroxide by analogy to the name phosphorus pentoxide. This compound has also been called phosphorosic oxide by Mellor [60] Although previous investigators[61] obtained a crystalline sublimate by heating the products of combustion of phosphorus, Thorpe and Tutton[62] were the first to show that this product is different from phosphorus pent-

[60] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1928, Vol. VIII

[61] P. Hautefeuille and A Perrey, *Compt rend.*, **99**, 33 (1884).

[62] T. E. Thorpe and A. E H Tutton, *J Chem. Soc.*, **49**, 833 (1886), *ibid*, **57**, 545 1890)· *ibid*, **59**, 1023 (1891).

oxide or trioxide. According to these authors, when phosphorus burns at a moderately high temperature in a limited supply of air, phosphorus tetroxide is formed to a considerable extent However, it is best prepared by heating phosphorus trioxide, P_4O_6, in a sealed, evacuated tube at 200 250° C. for several days. The resulting red-colored mixture of phosphorus tetroxide and red phosphorus (and/or lower oxides of phosphorus) can then be heated in such a way that the elemental phosphorus is sublimed to one end of the tube, which section is then sealed off. On heating the remaining oxides still hotter, the phosphorus tetroxide sublimes free from the small amount of residue and condenses to lustrous, transparent crystals that apparently belong to the cubic family [63]

Analyses[62,63] of crystals of phosphorus tetroxide correspond with the empirical formula, PO_2 Vapor density studies by two different investigators did not lead to the same results [63,64] West found molecular weights ranging from 440 to 480 in glass apparatus at 1400°C This corresponds approximately to the formula P_7O_{14} or P_8O_{16} The more recent investigators, Emmett and Shultz, found a much wider range of vapor densities, corresponding to molecular weights ranging from 293 to 721 Presumably, phosphorus tetroxide is a cage-like molecule, much larger than phosphorus pentoxide. The density of crystalline phosphorus tetroxide is 2.54 at 23°C The crystals are deliquescent in air and very soluble in water Although the composition of aqueous solutions of phosphorus tetroxide is not known, some chemical properties of these solutions, such as precipitation with various metal ions, have been investigated [62,63] Aqueous solutions of phosphorus tetroxide are difficult to oxidize to phosphoric acid

Preparation and Structure of Phosphorus Trioxide

Again, in analogy to phosphorus pentoxide, the compound with the empirical formula P_2O_3 is called phosphorus trioxide. It is also named phosphorous oxide or phosphorous anhydride It was not until the work of Thorpe and Tutton[62] that a reasonable preparative method was developed for this oxide by burning phosphorus under controlled conditions Improvements were made by later authors,[65] especially Wolf and Schmager, who concluded that the best results are obtained when white phosphorus kept at a temperature of 46–50°C is burned in a 17-mm. quartz

[63] C A West, *J. Chem Soc.*, **81**, 923 (1902)

[64] P H Emmett and J. F. Shultz, *Ind Eng Chem*, **31**, 105 (1939)

[65] J J Manley, *J Chem. Soc*, **121**, 331 (1922), L Woll and H Schmager, *Ber*, **62B**, 771 (1929).

tube in enriched air containing 75% total oxygen at a pressure of 90 mm. of Hg and a flow rate of 30 l./hr. Based on the phosphorus consumed, a yield of phosphorus trioxide of about 56% is obtained. Unpurified phosphorus trioxide always contains some dissolved phosphorus, even after repeated distillation, but this is removed by illuminating with a mercury arc to convert the phosphorus into the insoluble red variety, so that the remaining phosphorus trioxide can be recovered in pure form by distillation. A simple apparatus in which phosphorus trioxide is made in moderately high yields in a few minutes has also been described.[66]

Although a number of investigations[67] have been carried out on the factors affecting the proportions of the various oxides resulting from the oxidation of phosphorus by oxygen, it is quite apparent that much more work will have to be done before the optimum conditions for the formation of phosphorus trioxide are known. Factors needing further investigation are (1) temperature, (2) gas pressure and rate of flow, (3) amount and kind of gases other than oxygen, (4) distribution of the phosphorus, and (5) geometry of the system. Except perhaps for several recent unverified preparations[68] (and some extremely questionable early work), phosphorus trioxide has not been made by methods other than oxidation of phosphorus by oxygen.[69] In these recent studies the trioxide was incidentally reported as a product of (1) the reaction between tetramethylammonium sulfite and phosphorus trichloride in liquid sulfur dioxide and (2) the metathesis of phosphorus trihalides with organic metal oxides. In spite of some early work to the contrary, phosphorous acid apparently cannot be dehydrated to give its anhydride, phosphorus trioxide.[69]

Electron diffraction measurements show that phosphorus trioxide has the formula P_4O_6 in the vapor,[34,35] and that its structure is similar to that of phosphorus pentoxide except that the four peripheral oxygen atoms are absent. The structure is shown in Figure 6-1. The P-O distances are 1.65 ± 0.02 A by one group of investigators[34] and 1.67 ± 0.03 A by another.[35] These atom-center distances correspond to essentially no π-bonding. Vapor density measurements are in agreement with the fact that gaseous phosphorus trioxide is composed of P_4O_6 molecules.[62]

[66] H. Biltz and A. Gross, *Ber.*, **52B**, 762 (1919).

[67] For example, K. I. Zagvozdkin and N. A. Barilko, *J. Phys. Chem.* (*U.S.S.R.*), **14**, 505 (1940).

[68] G. Jander, H. Wendt, and H. Hecht, *Ber.*, **77B**, 698 (1944); H. H. Anderson, *J. Org. Chem.*, **19**, 1767 (1954); also private communication.

[69] For example, W. P. Jorissen and A. Tasman, *Rec. trav. chim.*, **48**, 324 (1929); L. Wolf, E. Kalachne, and H. Schmager, *Ber.*, **62B**, 1141 (1929); L. J. Chalk and J. R. Partington, *J. Chem. Soc.*, **1927**, 1930.

Raman data also have been interpreted[70,87] to mean that liquid phosphorus trioxide has the molecular formula P_4O_6, with T_d symmetry. It should also be noted that when liquid phosphorus trioxide is dissolved in molten naphthalene at 80°C., the freezing point lowering corresponds to a doubling of the empirical formula; *i.e.*, the correct formula is P_4O_6. Although only two Raman lines were found in the spectrum of solid phosphorus trioxide,[70] these shifts correspond to the two strongest lines of the Raman spectrum of the liquid, so that it is quite reasonable to assume that the molecular formula for crystalline phosphorus trioxide is also P_4O_6. Cryoscopic determination of the molecular weight of crystalline phosphorus trioxide dissolved in benzene led[62] to the double formula, P_4O_6

Air oxidation of phosphorus in carbon tetrachloride solution produced[71] a pale yellow, voluminous precipitate which was said to exhibit the empirical formula, P_2O_3. Upon being dried in a vacuum, the precipitate turned white. Presumably, this is a different modification than the usual phosphorus trioxide, since it was found to decompose at temperatures above 100°C. but did not melt at 23.8°C.—the melting point of the usual P_4O_6 variety of phosphorus trioxide. This material should be investigated further to determine whether or not it is homogeneous and has the composition alloted to it. Since it did not melt, one would guess that this reported other form of phosphorus trioxide is a three-dimensional polymer—perhaps a sheet polymer like the orthorhombic forms of phosphorus pentoxide.

Properties of Phosphorus Trioxide

The physical properties of phosphorus trioxide are given in Table 6-1, from which it can be seen that the solid melts at room temperature (23.8°C.) and has a boiling point of 175.4°C.[72] It is somewhat soluble in carbon disulfide and can be recrystallized from this solvent.[73]

White phosphorus is capable of dissolving in phosphorus trioxide to the amount of 1.7 g. of P per 100 g. P_4O_6 at 25°C.[73] As previously mentioned, this phosphorus can be removed by ultraviolet irradiation which converts the white phosphorus to the red form. It can also be removed by recrystallization from carbon disulfide.[73] The amount of phosphorus dissolved in P_2O_3 at room temperature corresponds to the empirical for-

[70] H. Gerding, H. von Brederode, and H. C. J. de Decker, *Rec. trav. chim.*, **61**, 549 (1942); H. Gerding, *J. chim. phys.*, **46**, 118 (1948)

[71] B. Blaser, *Ber.*, **64B**, 614 (1931)

[72] P. M. van Dorrmal and F. E. C. Scheffer, *Rec. trav. chim.*, **50**, 1100 (1931).

[73] C. C. Miller, *J. Chem. Soc.*, **1928**, 1847

mulas $P_{2.06}O_{3.00}$ or $P_{2.00}O_{2.91}$. It would be interesting to know whether the phosphorus is present as its own crystal, as in an eutectic mixture, or whether it forms a solid solution in the phosphorus trioxide. If it is the latter, the atomic configuration in such a crystalline solid solution is worthy of investigation. Presumably, from the fact that the phosphorus can readily be removed, the P_4 and P_4O_6 molecules each keep their own identity and do not interact.

Phosphorus trioxide is decomposed by heat according to the following equation.[62] The reaction proceeds slowly at temperatures near 210°C. and more rapidly at higher temperatures

$$P_4O_6 \xrightarrow{\Delta} 3\,PO_2 + P\,(red) \qquad (6\text{-}2)$$

The oxidation of phosphorus trioxide by oxygen has been investigated by a number of authors. When phosphorus trioxide made by the method of Thorpe and Tutton reacts in the vapor phase with oxygen, a glow is observed which is spectrally identical with the glow occurring during oxidation of elemental phosphorus.[74, 75] However, when the excess phosphorus is removed from the phosphorus trioxide, this glow no longer appears.[73] It should be noted that the glow of phosphorus trioxide containing excess phosphorus apparently also depends on the presence of a small amount of moisture in the system. Pure phosphorus trioxide seems to inhibit the glow of elemental phosphorus under certain conditions.[76] When phosphorus trioxide containing no free phosphorus is oxidized by a mixture of oxygen and ozone,[77] two molecules of P_4O_6 are oxidized for each mole of O_3 reacting. This means that oxygen, as well as ozone, takes part in the reaction. The oxidation product is a mixture of about 60 formula-wt.-% of PO_2, with the remainder being P_2O_5. When phosphorus trioxide containing free phosphorus is oxidized by oxygen in the presence of a small amount of water vapor, about five moles of P_4O_6 are oxidized for each mole of contained P_4. From this information and other experiments, Miller concludes that P_4O_6 is formed as an intermediate product in the oxidation of elemental phosphorus, but that, under most conditions, the phosphorus trioxide immediately decomposes so that the main product of

[74] A. Petrikaln, *Naturwissenschaften*, **16**, 205 (1928); C. C. Miller, *Proc. Roy. Soc. Edinburgh*, **46**, 76 (1926); H. J. Emeleus, *J. Chem. Soc.*, **127**, 1362 (1925); H. Rinde, *Chem. Zentr.*, **3**, 172 (1919); *Arkiv Kemi Mineral. Geol.*, **7**, No. 1 (7), 21 (1917–18).

[75] E. Scharpf, *Z. physik Chem.*, **62**, 179 (1908); "Über das Leuchten des Phosphors and einiger seiner Verbindungen," Thesis, Marburg, Germany, 1907, p. 26.

[76] C. C. Miller, *J. Chem. Soc.*, **1929**, 1823.

[77] C. C. Miller, *J. Chem. Soc.*, **1929**, 1829.

oxidation of elemental phosphorus is usually a mixture of phosphorus tetroxide and phosphorus pentoxide

The rate of absorption of oxygen by liquid phosphorus trioxide is said to be proportional to the square root of the oxygen pressure and to depend on the surface of the liquid P_4O_6 exposed, its rate of evaporation, and the temperature.[78] Considerable additional work is needed to elucidate thoroughly the kinetics of the oxidation of phosphorus trioxide

When P_4O_6 is shaken rapidly with an excess of cold water, the product is exclusively phosphorous acid.[79] Without shaking, two liquid layers are formed which are said to react with each other to give predominantly phosphoric acid and a yellow solid which may be P_2O (see below) or perhaps P_2H In hot water the reaction is very vigorous, giving rise to a number of products, including phosphine and a red product, probably red phosphorus. Phosphorus trioxide reacts violently with both chlorine and bromine to give the phosphoryl halides The reaction on admixture with iodine is much slower, with the product being an orange-red solid of unknown structure. When the two reactants are heated under pressure with a quantity of carbon disulfide, orange-red prisms of phosphorus diiodide separate out from the concentrated solution. It is assumed that the main reaction taking place in this case is the following

$$5\ P_4O_6 + 8\ I_2 \longrightarrow 4\ P_2I_4 + 6\ P_2O_5 \qquad (6\text{-}3)$$

Other Oxides of Phosphorus

By passing a mixture of oxygen and phosphorus pentoxide at low pressure (1 mm. of Hg) through a heated tube in which there is a silent electrical discharge, a blue-violet product[80] is obtained in a cooled section immediately after the region of discharge This product, which is believed to contain a peroxide of phosphorus, is stable in the absence of moisture for several days at room temperature It decomposes upon heating, and its aqueous solution behaves as a peroxyphosphoric acid If the empirical formula P_2O_6 is assumed for the phosphorus peroxide, the violet product contains about 2% of this peroxide

A number of early authors have discussed suboxides to which they have

[78] R Schenck, F. Mihr, and H Bathien, *Ber.*, **39**, 1506 (1906)

[79] L Wolf, W Jung, and M Tschudnowsky, *Ber*, **65B**, 488 (1932)

[80] P W. Schenk and H. Platz, *Naturwissenschaften*, **24**, 651 (1936). P. W. Schenk and H Rehaak, *Z anorg u allgem Chem*, **233**, 403 (1937)

assigned the formulas P_4O[80a] and P_2O[80b]. Later investigators[81] have sometimes been unable to repeat preparations of these "suboxides" and, when they made materials exhibiting the previously described properties, the reaction products were found to contain hydrogen. It has been postulated that these materials are simply mixtures of red phosphorus, the solid phosphorus hydrides, and various oxyacids of phosphorus. On the other hand, these materials (or similar materials) have been given the following empirical formulations[82] by some early workers P_4HO, P_4H_2O, P_5H_3O, and $P_5H_7O_2$.

From all of this literature, it appears that there are a number of products, the color of which varies from red to yellow, which contain some oxygen and hydrogen along with a large proportion of phosphorus. These materials are insoluble in water, alcohol, or ether and can be burned in air at elevated temperatures. Although it has been postulated that they are simple mixtures of known compounds,[81] this is thought not to be the case. Instead, such reaction products probably consist of mixtures of a number of structures of varying complexity in which there is a large proportion of P—P bonds, as well as some P—H and some P—O bonds. Since these products are insoluble, it will not be easy to determine their structure by the usual methods of polymer physics. Presumably, they are, at least in great part, amorphous to x-ray diffraction. An idea of the type of structures which might be involved can be formed from the structures suggested for the solid phosphorus hydrides on pages 215–219 and for amorphous red phosphorus on pages 117–118. The discussion concerning the structure of the lower oxyacids of phosphorus on pages 390–394 is also pertinent.

To recapitulate, there is no question but that finely divided yellow-

[80a] For P_4O see J. Pelouze, *Ann. chim. et phys.*, **50**, 83 (1832), M. Bengiezer, *Ann.*, **17**, 258 (1836), R. F. Marchand, *J. prakt. Chem.*, **13**, 442 (1838); U. J. J. Leverrier, *Ann. chim. et phys.*, **60**, 174 (1835), B. Remitzer and H. Goldschmidt, *Ber.*, **13**, 849 (1880), H. Biltz, *ibid.*, **27**, 1258 (1894), A. Michaelis and M. Pitsch, *ibid.*, **32**, 337 (1899), *Ann.*, **310**, 45 (1900), A. Michaelis and K. von Arend, *ibid.*, **314**, 259 (1901), E. Jungfleisch, *Compt. rend.*, **145**, 325 (1907), K. Weidner, "Über das Phosphorsuboxyd," Thesis, Erlangen, Germany, 1909.

[80b] For P_2O see A. Besson, *Compt. rend.*, **125**, 1032 (1897), *ibid.*, **132**, 1556 (1901), *Bull. soc. chim. France*, **25**, 582 (1900).

[81] C. H. Burgess and D. L. Chapman, *J. Chem. Soc.*, **79**, 1235 (1901), D. L. Chapman and F. A. Lidbury, *ibid.*, **75**, 973 (1899), K. C. Browning, *Proc. Chem. Soc.*, **17**, 243 (1901), A. Stock, *Chem. Ztg.*, **33**, 1354 (1901); L. J. Chalk and J. R. Partington, *J. Chem. Soc.*, **1927**, 1930.

[82] B. Franke, *J. prakt. Chem.*, **35**, 341 (1887), A. Gautier, *Compt. rend.*, **76**, 49, 173 (1873).

to-red-colored materials containing a large proportion of phosphorus plus some oxygen and hydrogen do exist. From the viewpoint of modern chemistry, the small amount of evidence available is most readily interpreted in terms of crosslinked polymers, the detailed structures of which are as yet undeciphered.

Phosphine Oxides[83]

The compounds, R_3PO, in which three alkyl and/or aryl radicals and an oxygen atom are attached to one phosphorus atom are called tertiary phosphine oxides. One of the simplest methods for their preparation is the direct oxidation of the corresponding phosphine Trialkylphosphines, from the lowest to the highest reported members, are readily oxidized by exposure to air or to oxygen However, triphenylphosphine is quite stable in air at room temperature. As might be expected, mixed arylalkylphosphines are intermediate in their susceptibility to oxidation Strong oxidizing agents, such as nitric acid or potassium permanganate, are needed to make phosphine oxides from tertiary arylphosphines, and such oxidants have also been employed in the preparation of alkylphosphines.

Organic dihalophosphines, R_3PX_2, are also readily converted to the corresponding phosphine oxides by oxidizing agents such as sulfur dioxide or even water. The esters of dialkyl- or diarylphosphinous acids react with alkyl halides to undergo isomerization to the phosphine oxide according to the following equation:

$$R_2POR' + R''X \longrightarrow [R_2(R'')P(OR')X] \longrightarrow R_2R''PO + R'X \qquad (6\text{-}4)$$

This reaction, which is a variation of the Michaelis-Arbusov rearrangement, is discussed, along with other similar rearrangements, in Chapter 7. There are a number of other ways of making tertiary phosphine oxides; indeed, Kosolapoff lists twelve preparative procedures in all!

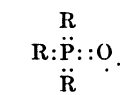
The phosphine oxides are all crystalline compounds with well-defined melting points. Thus, the crystals of trimethylphosphine oxide melt at 140°C., and the liquid boils at 214–215°C., while the melting point of triethylphosphine oxide is 46°C., and the boiling point is 240 ± 3°C. Triphenylphosphine oxide melts at 153°C. and boils at 360°C., and the crystals of tri(α-naphthyl)phosphine oxide melt at 341–342°C. The

[83] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, Chapt. 6, pp 98–120; R. B Fox and L B. Lockhart, *The Chemistry of Organophosphorus Compounds*, Naval Research Lab., Washington, D. C., 1948 (NLR Rept. C-3323).

relatively high melting point of trimethylphosphine oxide probably indicates some type of extremely close packing or secondary bonding, such as hydrogen bonding, in the crystal. Mixed methyl derivatives do not exhibit this unusually high melting point. Thus, dimethylethylphosphine oxide has a melting point of 73–75°C. and a boiling point of 223–225°C., and dimethylphenylphosphine oxide melts at 100°C. and boils at 300–308°C.

Tertiary phosphine oxides have the reputation of being the most stable chemical structures in the family of organophosphorus compounds.[83] The exceptions are (1) the benzyl derivatives which can lose the substituent radicals on fusion with alkali and (2) the esters of hydroxymethyl derivatives which suffer a similar fate on heating with aqueous alkali. As an example of this stability, triphenylphosphine oxide forms the meta nitro derivative exclusively on reacting with fuming nitric acid, and these nitro groups can be reduced to amino groups which may then be diazotized, acetylated, or otherwise reacted Throughout all of this rather drastic treatment, the group consisting of the phosphorus atom surrounded by the three carbon atoms and the oxygen is unaffected.

Tertiary phosphine oxides form a number of stable crystalline complexes with various acids. Examples of such acids are hydrochloric, hydrobromic, ferrocyanic, chlorauric, dichromic, cobalticyanic, and trichloroacetic In addition, crystalline hydrates, usually monohydrates but occasionally hemihydrates, are also known. Phosphine oxides form double salts with such halides as platinic and platinous chloride, cadmium iodide, zinc bromide, cobalt chloride, and mercuric chloride. The structure of these crystalline adducts is an interesting problem, since the phosphorus in tertiary phosphine oxides is undoubtedly present as a stable sp^3-hybrid. Presumably, the π-character in the four bonds surrounding the phosphorus atom is predominantly located in the P—O bond which thus would be expected to have the equivalent of somewhat more than one π-bond per σ-bond. Thus, this P—O bond should have at least as much and perhaps more multiple-bond character than the C=O bond in aldehydes and ketones, as indicated by the following structure:



(6-5)

Therefore, the explanation of the addition compounds of phosphine oxides should be exactly the same as the explanation for the similar addition

compounds which are so readily formed by aldehydes and ketones.[84] In the case of the adducts with salts, the oxygen atom undoubtedly enters the coordination sphere of the metal atom of the salt. Presumably, the adducts with acids are primarily held together by hydrogen bonds, although the formation of an hydroxyl radical (with the concomitant transfer of a positive charge to the phosphorus of the phosphine oxide, and perhaps even to the carbon of an aldehyde or ketone, the charge being counterbalanced by the anion of the acid) is also a possibility. It is obvious that the use of *d*-orbitals in the σ-bond structure of the adducts of tertiary phosphine oxides, as has been implied in suggested sp^3d-structures,[85] is unsound for phosphorus although it might be possible for antimony and perhaps even arsenic.

Two tertiary phosphine oxides based on three different organic radicals have been resolved into their optical isomers.[86] To do this in one case, phenylmethylethylphosphine oxide was combined with *d*-bromocamphorsulfonic acid to give the adduct which, after repeated crystallization from ethyl acetate yielded the optically pure (*d*-phenylmethylethylphosphine oxide)-(*d*-bromocamphorsulfonic acid) adduct. This compound in aqueous solution exhibited an optical rotation of $[M]_D = +313°$ which fell to $+306°$ on the addition of sodium hydroxide, with no indication of even partial racemization. It was concluded that, since ammonium *d*-bromocamphorsulfonate at an equivalent concentration in water has $[M]_D = +267°$, the free phosphine oxide would exhibit a value of $[M]_D = +39°$ to $+46°$, depending on the conditions. By passing dry ammonia through a benzene solution of the adduct of the phosphine oxide and bromocamphorsulfonic acid, the free phosphine oxide was obtained through precipitation of the insoluble ammonium bromocamphorsulfonate. It was found that the resulting free *d*-phosphine oxide had high optical stability and could be distilled under reduced pressure without racemization. This is what would be expected, since there is no obvious mechanism by which the phosphine oxide could racemize without undergoing decomposition. The crystalline, deliquescent phosphine oxide was found to show a value of $[M]_D = +38°$ in neutral aqueous solution, $+47°$ in benzene solution, and $+40°$ in water containing a mole equivalent of hydrochloric acid.

[84] For example, see W. R. Brode, *Chemical Spectroscopy*, 2nd ed., John Wiley & Sons, Inc., New York, 1943, pp. 221-22, A. Rosenheim and W. Stellmann, *Ber.* **34**, 3377 (1901), P. Pfeiffer, *Ann.*, **376**, 296 (1910), B. N. Menschutkin, *Izvest. St. Petersburg Polytech.*, **4**, 101 (1905), *ibid.*, **6**, 39, 101 (1906), *J. Russ. Phys.-Chem. Soc.*, **44**, 1929 (1912), H. Lewy, *J. prakt. Chem.*, **37**, 480 (1846).

[85] F. G. Mann, *J. Chem. Soc.*, **1945**, 65.

[86] J. Meisenheimer, *Ber.*, **44**, 356 (1911), *Ann.*, **449**, 224 (1926).

The other phosphine oxide to have been resolved optically is phenylbenzylmethylphosphine oxide, which was obtained as both the *d* and *l* forms by recrystallization with *d*-camphosulfonic acid. In this case, the *d*-phosphine oxide in aqueous solution had $[M]_D = +162°$; in water containing a mole equivalent of hydrochloric acid, the value increased to $+168°$, but in chloroform $[M]_D = -17°$ The *l*-phosphine oxide in water containing a mole equivalent of hydrochloric acid had $[M]_D = -167°$ The phenomenal change in the optical rotation constant of *d*-phenylbenzylmethylphosphine oxide when going from water to chloroform has not been explained[85] in the literature but may be due to hydrogen bonding in the aqueous systems. This suggestion is equivalent to the formation of an OH group from the oxygen of the tertiary phosphine oxide, as postulated for the phosphine oxide adducts

PHOSPHORUS SULFIDES

When white phosphorus and sulfur are mixed together at temperatures below about 100°C, no reactions take place, but solid solutions are formed The phase diagram[87] obtained under these conditions is shown in Figure 6-5, where it can be seen that the eutectic between the phosphorus-rich

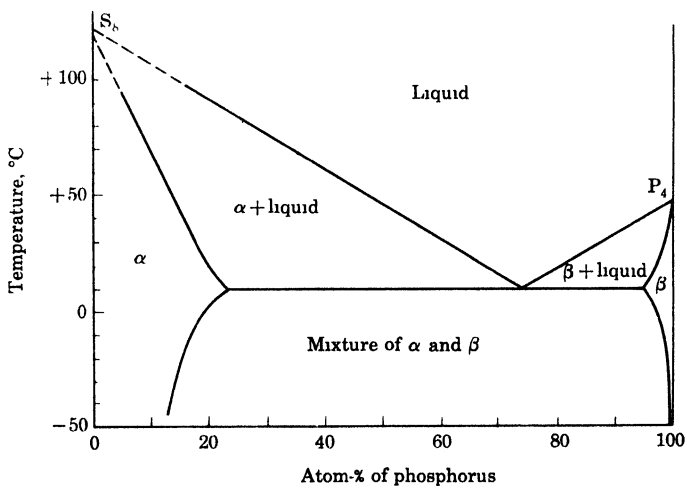


Fig 6-5 The system phosphorus-sulfur, below the temperature of reaction (about 100°C) α is a sulfur-based solid solution and β is one based on phosphorus

[87] V. V Illarionov and T I Sokolova, *Izvest Akad. Nauk S S S R, Fiz Khim*, **21**, 153 (1952), R Boulouch, *Compt. rend*, **135**, 165 (1902)

and the sulfur-rich solid solutions appears at 74 atom-% phosphorus and a temperature of 9.8°C. In this phase diagram there are two regions of solid solution; one of them marked α which has the same crystal structure as the S_8 molecule, and the other marked β, which exhibits the crystal structure of the P_4 molecule At temperature below 9.8°C. there is an extended region in which the α and β solid solutions crystallize out together.

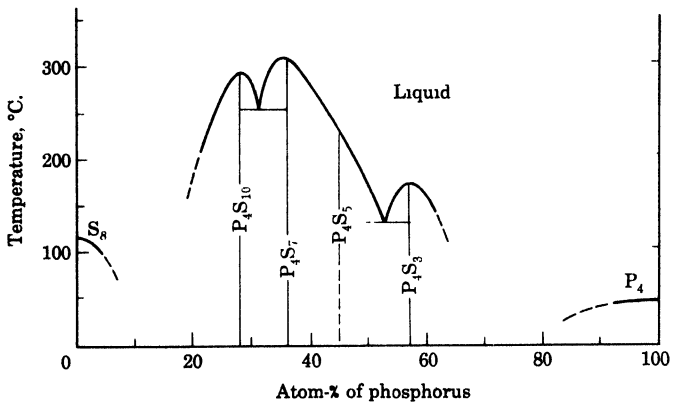


Fig 6-6. Melting-point diagram[a] for the system, phosphorus-sulfur, after reaction has occurred The compound P_4S_5 either decomposes in the solid state to P_4S_7 and P_4S_3 or melts incongruently

As was noted by the earliest investigator[2] of the phosphorus-sulfur system, there is a vigorous exothermic reaction between sulfur and phosphorus at temperatures above about 100°C. From this reaction, several crystalline compounds—P_4S_3, P_4S_5, P_4S_7, P_4S_{10}, and perhaps $(P_2S_3)_n$—are obtained. Although the early literature describes other alleged phosphorus-sulfur compounds, they will not be discussed here, since they have been shown to consist of mixtures of the presently recognized compounds In Figure 6-6 the available data[88,89] on the phosphorus-sulfur system at equilibrium are interpreted in terms of a phase diagram showing the three regularly melting crystalline phosphorus sulfides. This phase diagram is only approximate, and the data should be carefully re-examined.

In addition to the four or five crystalline phosphorus sulfides,[89] there also appear to be amorphous combinations of these elements—combina-

[88] H Giran, *Compt rend.*, **142**, 398 (1906)

[89] J C Pernert and J. H Brown, *Chem Eng News*, **27**, 2143 (1949)

tions which must be classed as high polymers. In the following sections, the crystalline phosphorus sulfides will be discussed individually, and then the available information on polymeric P-S structures will be presented.

Phosphorus Pentasulfide

Modern commercial preparation of phosphorus pentasulfide is carried out by reacting white phosphorus and elemental sulfur with each other in a continuous process.[90] It is also made in commercial quantities by heating elemental sulfur with red phosphorus in a batch process. If the molten phosphorus sulfide, as prepared commercially, is properly cooled, it will consist almost completely of crystalline P_4S_{10}. Apparently some of the early commercial preparations (around 1910) were either insufficiently heated so that they consisted of a mixture of the α- and β-phases of the mixed crystals between white phosphorus and α-sulfur, or they were quickly quenched so that polymeric phosphorus-sulfur compounds resulted, since there are references in the literature of that time to the fact that commercial phosphorus pentasulfide exhibited different properties from those of the accepted crystalline variety. It is interesting to note that preparation of phosphorus pentasulfide from ferrophosphorus and pyrites (FeS_2) has been described.[91]

The accepted laboratory preparative method[12] is to heat the correct stoichiometric amounts of phosphorus and sulfur, with a 1% excess of sulfur, in a closed, previously evacuated, glass tube at 700°C. and then to cool slowly. Since the pressure in the heated tube may amount to several atmospheres, thick-walled glass that has been properly sealed together is recommended. Phosphorus pentasulfide can also be made in solution.[92] Thus, P_4S_3 and sulfur can be reacted together in the presence of naphthalene; or, alternately, a solution containing yellow phosphorus and elemental sulfur in carbon disulfide can be added to naphthalene and the temperature slowly raised to 175–200°C. Upon cooling, crystals of phosphorus pentasulfide are formed. Purification of either commercial phosphorus pentasulfide (exhibiting a good x-ray pattern with little indication of amorphous material) or a laboratory preparation is effected by repeated recrystallization from hot carbon disulfide solution. The re-

[90] O. C. Jones, U. S. Pat. 2,569,128 (1951), Brit. Pat. 652,514 (1951, assigned to Monsanto Chemical Co.)

[91] V. V. Illarianov, T. I. Sokolova, and S. I. Vol'fkovich, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1945**, 94.

[92] J. Mai, *Ber.*, **44**, 1229 (1911), *ibid.*, **44**, 1725 (1911).

sulting phosphorus pentasulfide is obtained as beautiful, pale yellow crystals which melt to a red-brown liquid at 286–290°C

X-ray diffraction study[93] of crystalline P_4S_{10} shows that it has essentially the same structure as P_4O_{10}, with S substituting for O The dimensions of the P_4S_{10} molecule are as follows P-S distance to the shared sulfur is 2.09 ± 0 03 Å , to the isolated sulfur is 1.96 ± 0 03 Å while the P—S—P and S—P—S angles are all tetrahedral, 109 5°. As was the case for P_4O_{10}, the P—S bond to the sulfur atoms shared between adjacent PS_4 tetrahedra is considerably longer than the P—S bond to the isolated sulfur

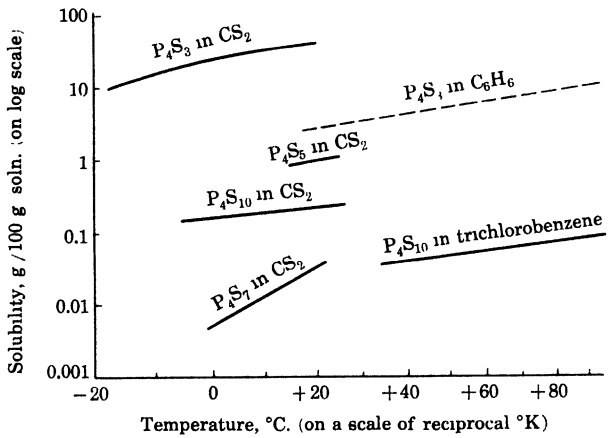


Fig 6-7 Some approximate solubility data on the phosphorus sulfides

atoms. However, there appears to be less total π-bonding than in P_4O_{10} since the P-S distance to the shared sulfur corresponds to essentially no π-bonding, and the P-S distance to the isolated sulfur corresponds to only 0.3–0.4 π-bonds per σ-bond, assuming that the mean values of the measured distances are correct

Phosphorus pentasulfide exhibits a triclinic crystal with two P_4S_{10} molecules per unit cell. Colligative measurements of molecular weight in boiling carbon disulfide solution indicate that the P_4S_{10} formulation for crystalline phosphorus pentasulfide is correct.[6] The solubility of phosphorus pentasulfide in carbon disulfide is shown in Figure 6-7.

The vapor pressure[94] of phosphorus pentasulfide is given, at least to a first approximation, by the following equation.

[93] A. Vos and E H Wiebenga, *Acta Cryst* , **8**, 217 (1955)

[94] R. W Atteberry, M. L Salutsky, J W. Lefforge, and H C Lottes, unpublished information from the Monsanto Chemical Company

$$\log p_{mm} = -1940/T + 9.17 \qquad (6\text{-}6)$$

This corresponds to a heat of vaporization of 22.6 kcal./mole. Vapor density measurements[7,8] indicate that the vapor of phosphorus pentasulfide is extensively decomposed, even at 600°C., which is very close to the boiling point of 513-515°C. Measured molecular weights are 208 at 600°C., 185 at 700°C., 144 at 800°C., 136 at 900°C., and 133 at 1000°C. These values should be compared to the P_4S_{10} formula weight of 444.

When the vapor of phosphorus pentasulfide is condensed on an extremely cold surface, such as one cooled by liquid air, a green solid results.[6] Indeed, there are a number of reports in the literature of greenish vapors of various phosphorus sulfides. The green color of the quickly frozen phosphorus pentasulfide vapor—a material which turns yellow when the temperature is raised above −100°C.—implies that the vapor is not simply a mixture of elemental sulfur and tetraphosphorus heptasulfide or phosphorus sesquisulfide but, instead, may contain some free radicals. If this is so, the work of Stock and Thiel in 1905 may be an early example in which free radicals were frozen from the vapor state. It should be noted that phosphorus pentasulfide can be purified by distillation, and that a good crystalline product can be obtained if the distilled liquid is allowed to crystallize slowly. Obviously, the dissociation of the vapor—regardless of its character—is readily reversible.

TABLE 6-2
Products from Hydrolysis of the Phosphorus Sulfides

	Percentage of total phosphorus recovered								
	In alkaline solutions of [a]			In acidic solutions of [a]			In solutions of [b]		
Product	P_4S_3	P_4S_7	P_4S_{10}	P_4S_3	P_4S_7	P_4S_{10}	P_4S_3	P_4S_7	P_4S_{10}
Phosphine, PH_3	5	3		3			3	0	0
Hypophosphorous acid, H_3PO_2	15	2	10	1	10		38	24	0
Phosphorous acid, H_3PO_3	75	38		39	0		49	22	0
Phosphoric acid, H_3PO_4	0	57	80	57	85		6	51	100

[a] By Treadwell and Beeli.[98]
[b] By Pernert and Brown.[89]

As shown in Table 6-2, phosphorus pentasulfide hydrolyzes in both acidic and basic solution to give predominantly hydrogen sulfide and phos-

phoric acid according to the following equation. Presumably there are a number of intermediates which have not been isolated.

$$P_4S_{10} + 16\ H_2O \longrightarrow 4\ H_3PO_4 + 10\ H_2S \qquad (6\text{-}7)$$

Phosphorus Disulfide

Although the phosphorus sulfide with the empirical formula PS_2 has been described by a number of authors, it has been shown by Stock[8] that this compound does not appear in the P—S phase diagram. However, crystals alleged to have this empirical composition have been made in carbon disulfide by the action of light on mixtures of phosphorus and sulfur[95] or mixtures of phosphorus sesquisulfide and sulfur.[96] The question of the existence of crystals having a PS_2 composition could be easily settled by an x-ray powder pattern

Tetraphosphorus Heptasulfide

The compound having the formula P_4S_7 has been called tetraphosphorus heptasulfide or phosphorus tetritaheptasulfide. It is prepared by heating a mixture of the stochiometric amounts of phosphorus and sulfur plus 5% of P_4S_3 in a hard glass tube until distillation becomes evident.[11] Since P_4S_7 is the least soluble of the crystalline phosphorus sulfides in carbon disulfide, the other phosphorus sulfides present in the mixture prepared as described above can be extracted. The resulting residue of P_4S_7 is then purified by recrystallization from the same solvent. Another preparative method for tetraphosphorus heptasulfide consists of heating stoichiometric amounts of P_4S_3 and P_4S_{10} in carbon disulfide at 100°C.[9, 11]

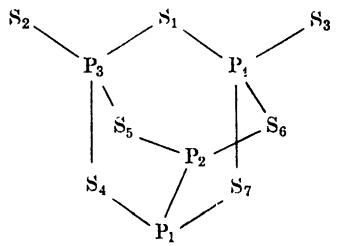
After being purified by recrystallization, tetraphosphorus heptasulfide is obtained as transparent prisms which are nearly colorless or pale yellow. As shown by Figure 6-7, it is the least soluble of the crystalline phosphorus sulfides. It is also the most dense.

At temperatures within several hundred degrees of the boiling point at 523°C., the vapor of tetraphosphorus heptasulfide consists of P_4S_7 molecules. However, at higher temperatures, the vapor undergoes considerable dissociation. Thus, at 700°C. the observed vapor density corresponds to a molecular weight of 337, at 800°C. the molecular weight is 202, at 900°C. the molecular weight is 179, and at 1000°C. the molecular weight is 167. These values should be compared with the formula weight

[95] R. Boulouch, *Compt. rend.*, **138**, 363 (1904).
[96] E. Dervin, *Compt. rend.*, **138**, 366 (1904).

of 348 for P_4S_7. In an atmosphere of CO_2, P_4S_7 can be distilled at ordinary pressures without appreciable decomposition.

The structure of P_4S_7 has been determined by x-ray diffraction.[93,97] This molecule has a rather unusual structure, as shown below.



P_3-S_2 = P_4-S_3 = 1.95 ±0.01 A.
all other P-S = 2.08 ±0.02 A.
P_1-P_2 = 2.35 ±0.01 A.
$\angle S_2P_3S_1 = \angle S_3P_4S_1 = 107°$
$\angle S_2P_3S_4 = \angle S_3P_4S_7 = 114°$ (6-8)
$\angle S_4P_3S_5 = \angle S_7P_4S_6 = 103°$
all other $\angle$SPS = ca. 109.5°
$\angle SP_1P_2 = \angle SP_2P_1 = 102°$

In this cage-like structure, two five-membered rings and two six-membered rings are fused together. Five of the sulfur atoms are in bridging positions, being shared between phosphorus atoms, while the two remaining sulfurs are associated with only one phosphorus atom apiece. Moreover, two phosphorus atoms are linked directly to each other. These two phosphorus atoms are triply connected, whereas the other two phosphorus atoms are tetrahedrally connected to their neighboring atoms. As is the usual case, the triply connected phosphorus atoms exhibit no π-bonding, whereas the P-S distance between the quadruply linked phosphorus and the bridging sulfur corresponds to 0.1 π-bond per σ-bond, and the P-S distance to the isolated sulfur atom corresponds to 0.4–0.5 π-bond per σ-bond. This molecule is particularly interesting, in that it demonstrates three regularities observed in the chemistry of phosphorus. These regularities are (1) there is little or no π-bond shortening for triple connected phosphorus atoms, (2) there is some π-bond character in each σ-bond leading from a quadruply connected phosphorus atom, and (3) for a quadruply connected phosphorus serving as a branching point, the π-bond shortening predominates in the bond to the isolated atom (S, in this case).

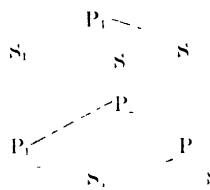
Tetraphosphorus heptasulfide reacts more rapidly with moisture than do the other crystalline phosphorus sulfides. When exposed to moist air, it slowly gives off hydrogen sulfide. As shown in Table 6-2, tetraphosphorus heptasulfide hydrolyzes with water. The rate of hydrolysis is moderately slow for cold water but very fast in boiling water. In addition to the products of hydrolysis shown in Table 6-2, it has also been said that hydrogen, H_2, is produced from the reaction of P_4S_7 with water

[97] A. Vos and E. H. Wiebenga, *Acta Cryst.*, **9**, 92 (1956).

Tetraphosphorus Pentasulfide

The compound having the formula P_4S_5 is the least well known of the generally accepted phosphorus sulfides. It is called tetraphosphorus pentasulfide or phosphorus tetritapentasulfide. It is formed by allowing a solution of the stoichiometric amounts of P_4S_3 and sulfur with a trace of iodine as catalyst to be exposed to diffuse daylight for several days [95,98] The P_4S_5 is obtained as bright yellow crystals which can be recrystallized from carbon disulfide

Molecular weight measurements in boiling carbon disulfide correspond to the P_4S_5 formula The structure of this molecule has recently been determined from x-ray diffraction data and is shown below [99]



P_1-S_1 = 2.19 ± 0.03 A.
P_4-S_2 = P_4-S_4 = 2.14 ± 0.03 A
P_3-S_4 = P_1-S_1 = P_2-S_2 = P_3-S_3 = P_4-S_1 = 2.09 ± 0.03 A
P_3-S_5 = 1.94 A
P_1-P_2 = P_2-P_3 = 2.21 ± 0.03 A.

$\angle S_5P_3P_2 = 128°$, $\angle S_5P_3S_4 = 114°$, $\angle S_4P_3S_4 = 111°$, $\angle S_1P_4S_3 = \angle P_1S_1P_4 = \angle S_1P_1S_1 = \angle S_2P_2P_1 = \angle S_3P_3P_2 = \angle S_4P_3S_5 = 107°$, $\angle S_1P_4S_2 = \angle S_2P_1S_3 = \angle P_2S_2P_4 = \angle P_3S_3P_4 = \angle S_2P_2P_3 = 100°$; $\angle P_1P_2P_3 = \angle P_2P_3S_1 = \angle P_3S_1P_1 = \angle S_4P_1P_3 = 87°$ (6-9)

In the cage-like structure of P_4S_5, two five-membered and a four-membered ring are fused together. Three of the phosphorus atoms are triply connected and one is quadruply connected to the neighboring atoms The bond from the quadruply connected phosphorus to the isolated sulfur atom (P_3—S_5) exhibits about 0.5 π-bond per σ-bond, whereas the other P—S bonds have 0.1 π-bond per σ-bond or less π-character The P-P atom-center distances correspond to a σ-bond with no π-character It is interesting to note that the bonds to the sulfur (S_4) in the four-membered ring are abnormally long by about 0.08 A., perhaps because of strain in the ring. The bond angles in this ring are all smaller than the 90° corresponding to a p^3-hybrid. Indeed, the quadruply connected phosphorus atom exhibits an odd assortment of bond angles—87° in the ring plus angles of 107°, 107°, 111°, 114°, and 128°.

[98] W. D. Treadwell and C. Beeli, *Helv. Chim. Acta*, **18**, 1161 (1935)
[99] S van Houten and E. H Wiebenga, *Acta Cryst*, **10**, 156 (1957)

Tetraphosphorus pentasulfide decomposes on heating so that the following dissociation occurs [98]

$$2\ P_4S_5 \longrightarrow P_4S_3 + P_4S_7 \qquad (6\text{-}9)$$

Very pure P_4S_5, therefore, melts over the wide range of 170–220°C., which means that at 170°C., the rate of decomposition is quite rapid. Because of this decomposition, tetraphosphorus pentasulfide does not appear in the phase diagram shown in Figure 6-6 except as a possible solid component with an unknown temperature of transition to the mixture of P_4S_3 and P_4S_7 shown in equation 6-9. This transition may, of course, simply be incongruent melting.

Phosphorus Sesquisulfide

The compound with the formula P_4S_3 is called phosphorus sesquisulfide, tetraphosphorus trisulfide, and phosphorus tetratrisulfide. It is readily formed by heating a stoichiometric mixture of red phosphorus and powdered sulfur with an excess of red phosphorus in a glass tube gradually to 100°C. and then more strongly, especially near the surface of the mixture, until the reaction starts and spreads throughout the mixture.[10] Naturally, the preparation must be carried out in an atmosphere of carbon dioxide or in an evacuated tube to avoid air oxidation. Following the exothermic reaction, the mixture should be heated strongly until distillation begins, in order that a minimum of other sulfides be present. Purification can be effected by extracting with carbon disulfide in which P_4S_3 is more soluble than the other crystalline phosphorus sulfides. It can also be distilled in an atmosphere of carbon dioxide.

Two unusual preparations of phosphorus sesquisulfide should also be mentioned here.[100] One of them consists of the action of gaseous phosphine on elemental sulfur to form the phosphorus sulfide plus gaseous hydrogen sulfide. The second similar reaction is between phosphine and thionyl chloride, $SOCl_2$, or pyrosulfuryl chloride, $S_2O_5Cl_2$.

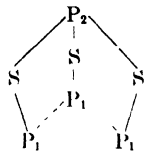
Because of its use in the manufacture of matches, phosphorus sesquisulfide is made on a commercial scale.[101] This is done by running molten white phosphorus into molten sulfur contained in a stirred cast-iron vessel. The reaction temperature is maintained at 320–380°C. by controlling the rate of addition of the white phosphorus. When addition is complete,

[100] L. Delachaux, *Helv. Chim. Acta*, **10**, 195 (1927); A. Besson, *Compt. rend.*, **122**, 467 (1896), *ibid.*, **123**, 884 (1896); *ibid.*, **124**, 401 (1897).

[101] A. H. Loveless, *P. B. Report No. 34740* or *B.I.O.S. Report No. 562* (Item 22), 1946.

the batch is maintained in this temperature range by external heating for several hours. The product is purified by vacuum distillation and/or by washing with either water or a dilute bicarbonate solution. Vacuum drying at 40–50°C. follows the washing process. Phosphorus sesquisulfide can also be made in a continuous process.[90]

The structure of phosphorus sesquisulfide has been determined by x-ray diffraction.[102,103] As shown below, there is a strained ring composed of three phosphorus atoms, with each of these phosphorus atoms being bonded through a separate sulfur atom to a third phosphorus, so that the over-all structure is in the form of a cage



$$\begin{aligned} P_1\text{-}P_1 &= 2.24 \text{ A.}^{102} \text{ or } 2.17 \text{ A}^{103} \\ P_1\text{-}S = P_2\text{-}S &= 2.11 \text{ A}^{102} \text{ or } 2.08 \text{ A}^{103} \\ \angle P_1P_1P_1 &= 60° \\ \angle P_1SP_2 &= 102° \\ \angle SP_1P_1 &= 103° \\ \angle SP_2S &= 100° \end{aligned} \qquad (6\text{-}10)$$

All of the atom-center distances in this structure correspond to the expected σ-bond distances with essentially no π-bonding. Phosphorus sesquisulfide, and white phosphorus, P_4, are the only two known compounds of phosphorus in which three-membered strained rings are found.

The molecular weight of P_4S_3 has been determined in boiling benzene and found to range from 228 to 264, values which should be compared with the P_4S_3 formula weight of 220. As indicated by the vapor density, gaseous P_4S_3 decomposes at elevated temperatures. Vapor density molecular weights are 219 at 700°C., 202 at 800°C., 182 at 900°C., and 179 at 1000°C.

Phosphorus sesquisulfide is generally the most soluble of the crystalline phosphorus sulfides. As well as being soluble in carbon disulfide and benzene, it can also be dissolved in phosphorus trichloride and in thiophosphoryl chloride. Under ordinary conditions, phosphorus sesquisulfide is unaffected by exposure to the atmosphere. It also does not react noticeably with water at ordinary temperatures. At 40–50°C. it oxidizes slowly with phosphorescence in air. At this temperature and at higher tempera-

[102] S. Houten, A. Vox, and G. A. Wregers, *Rec. trav. chim.*, **74**, 1167 (1955); also see O. Hassel and A. Pettersen, *Tids. Kjemi, Bergvesen Met.*, **1**, 57 (1941), who obtained P—P = P—S = 2.15 A.

[103] Y. C. Leung, J. Waser, and L. R. Roberts, *Chemistry & Industry*, **1955**, 948.

tures, the oxidation appears to proceed by a branching-chain mechanism,[75] with a higher and lower limit of oxygen pressure for the appearance of a greenish glow during oxidation. At temperatures above about 100°C., phosphorus sesquisulfide burns with a flame in air.

The final products of the reaction of phosphorus sesquisulfide with boiling water, in which the decomposition proceeds very gradually, are listed in Table 6-2. It should be noted that this sulfide is believed to hydrolyze primarily to a mixture of hypophosphorous and phosphorous acids. In the cold, hydrochloric and sulfuric acids have scarcely any action on phosphorus sesquisulfide, but nitric acid causes the formation of

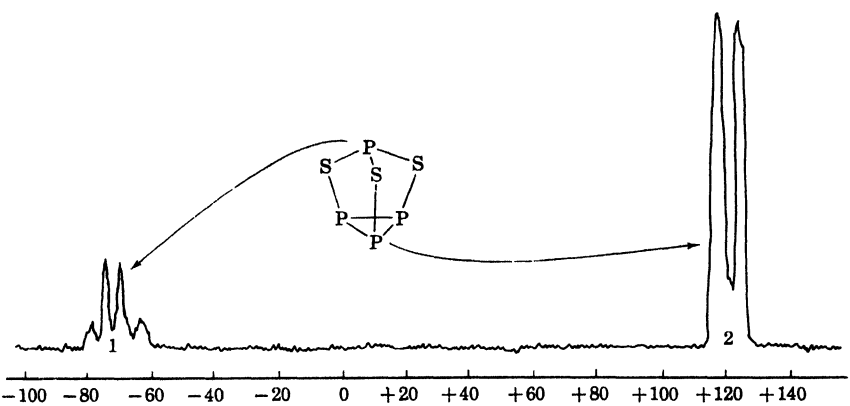


Fig 6-8 Nuclear magnetic resonance spectrum of phosphorus sesquisulfide at 7140 gauss and 12 3 megacycles

elementary sulfur and various oxyacids of phosphorus. Cold *aqua regia* is capable of oxidizing and dissolving solid phosphorus sesquisulfide completely to form phosphoric and sulfuric acids. In the finely divided state, phosphorus sesquisulfide reacts rapidly with solutions of potassium hydroxide to give gaseous phosphine and hydrogen, as well as sulfide, hypophosphite, and phosphite ions in solution Phosphorus sesquisulfide can be dissolved with reaction in liquid ammonia to give a reddish brown solution which becomes dark red with time and finally is transformed into a brown jelly. Upon evaporation of the ammonia and the phosphine resulting from the reaction, a viscid mass containing thiophosphates and other compounds remains. Phosphorus sesquisulfide also can be dissolved in ether and alcohol with reaction

In carbon disulfide solution, phosphorus sesquisulfide undergoes a number of unusual reactions. In the absence of oxygen and water, solutions of P_4S_3 in CS_2 are very stable. However, upon exposure to the air, oxygen is absorbed with the formation[13] of $P_4O_4S_3$. The $P_4O_4S_3$ appears as a yellowish precipitate which is formed rapidly in the P_4S_3 solution. Iodine acts on phosphorus sesquisulfide in carbon tetrachloride solution in two ways,[98] as indicated by the following equations

$$7\ P_4S_3(\text{in } CS_2) + 24\ I_2(\text{in } CS_2) \longrightarrow 16\ PI_3(\text{in } CS_2) + 3\ P_4S_7 \qquad (6\text{-}11)$$

$$P_4S_3 + 1\ I_2 \longrightarrow P_4S_3I_2 \qquad (6\text{-}12)$$

Another crystalline compound, $P_4S_3I_2$, is said to result from a reaction between P_4S_3 and I_2 in carbon disulfide solution. It is believed that the reaction between bromine and phosphorus sesquisulfide leads primarily to phosphorus tribromide and phosphorus pentasulfide.[98] As previously mentioned, P_4S_3 and sulfur in carbon disulfide react to give crystals of P_4S_5. It has been reported that precipitates with empirical formulas, P_8S_{11} and PS_2, can also be obtained by reacting phosphorus sesquisulfide and elementary sulfur in carbon disulfide.[96] The P_8S_{11} precipitate is believed to be a mixed crystal (or other mixture) of P_4S_3 and $(PS_2)_x$.

Phosphorus sesquisulfide may be separated from phosphorus pentasulfide by vacuum distillation. The sesquisulfide can also be distilled in a vacuum from mixtures of P_4S_3 and P_4S_7. However, sulfur is the first to be volatilized from mixtures of phosphorus sesquisulfide and elementary sulfur in a vacuum.

Polymeric Phosphorus Sulfides

It is well known that there is a plastic-elastic form of sulfur, but the fact that considerable amounts of phosphorus can be incorporated into such sulfur has been discussed very little. In this section it will be shown that polymeric structures are present in melts (and in amorphous solids obtained by quenching these melts) in the composition range $0 < P/S$ mole ratio $<$ *ca.* 0.4. However, before discussing the phosphorus-sulfur system, it is necessary to review briefly the available information on the polymeric nature of liquid sulfur and of the sulfur obtained by quenching the liquid.

As shown in Figure 6-9, the viscosity[104] of molten sulfur goes through a pronounced maximum at about 170°C. When the liquid at temperatures in the range of 160–250°C. is rapidly chilled, a highly plastic elastomeric

[104] R. F. Bacon and R. Fanelli, *J. Am. Chem. Soc.*, **65**, 639 (1943), R. E. Powell and H. Eyring, *ibid.*, **65**, 648 (1943).

form of amorphous sulfur (called $S\mu$) is obtained This plastic sulfur can be drawn into fibers which possess considerable tensile strength. X-ray examination[105] of these stretched fibers has revealed a fiber pattern

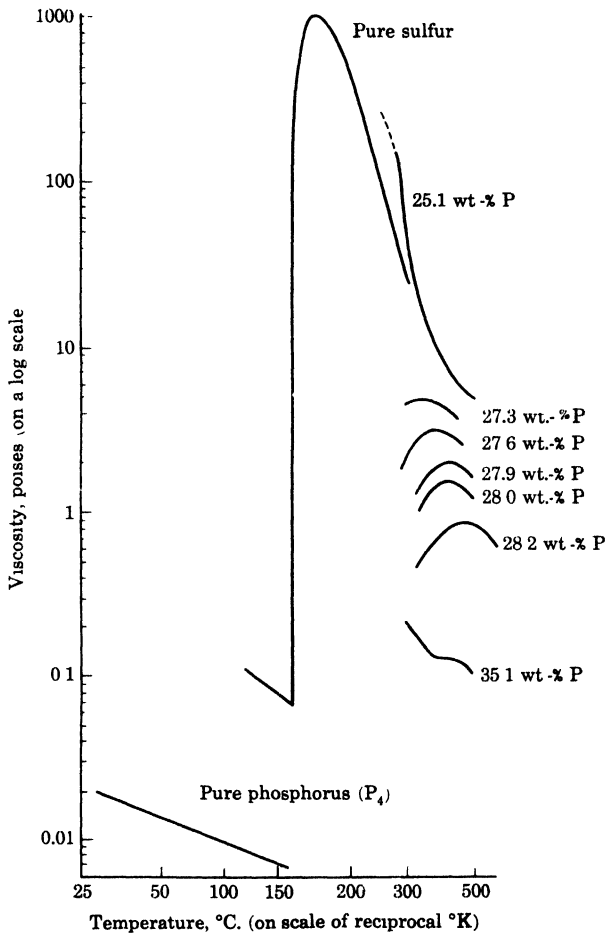


Fig. 6-9 Variation of viscosity with temperature for pure sulfur, pure phosphorus, and various phosphorus-sulfur mixtures. (It should be noted that for such mixtures atom-percentages are only slightly larger than weight-percentages)

corresponding to a unit cell containing approximately 112 atoms, with a repeat distance along the fiber axis of 9.26 A. In view of the knowledge of

[105] K. Meyer and Y. Go, *Helv. Chim Acta*, **17**, 1081 (1934).

other stretched fibers, the fibrous nature of plastic sulfur must certainly be interpreted as being indicative of the presence of long chains of sulfur atoms. Pauling[106] has suggested that the repeating unit in the chains of sulfur atoms found in plastic sulfur is a two-turn spiral of seven atoms

The composition of molten sulfur has been calculated as a function of temperature by considering quite a large body of experimental data, and the results of a recent set[107] of these calculations are shown in Figure 6-10, from which it can be seen that the long chain sulfur starts to form at a

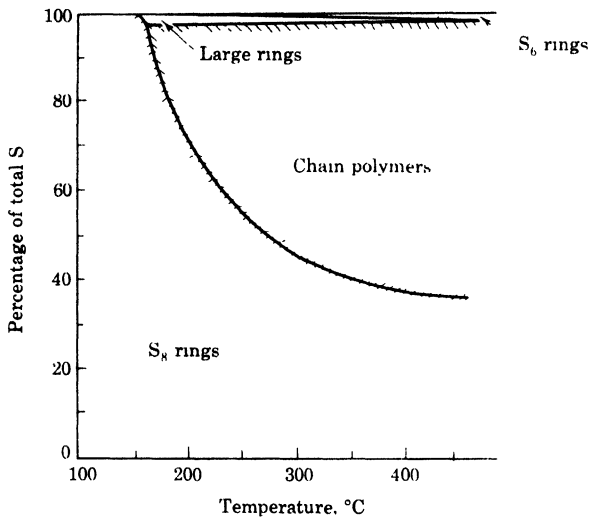


Fig 6-10. An area plot showing the composition of liquid sulfur as a function of temperature

critical temperature of 159°C. and increases with rising temperature, leveling off at about 60% of the total sulfur at a temperature of 350–400°C. Several estimates have also been made of the average chain length of the sulfur polymer. Since 0.02% of iodine reduces the maximum chain length by approximately 16-fold at the viscosity maximum, the original chain length of the sulfur can be calculated on the basis that iodine is a chain breaker which acts by the mechanism of attaching a single iodine atom at each broken end of the sulfur chain. From this reasoning, it appears[107] that the number average chain length of the sulfur polymer

[106] L. Pauling, *Proc. Natl. Acad. Sci., U. S.*, **35**, 495 (1949)
[107] G. Gee, *Science Progr.*, **170**, 193 (1955).

passes through a maximum of about 10^6 atoms per chain at a temperature of about 170°C. Although the accuracy was insufficiently high for a precise determination, paramagnetic resonance measurements[108] on liquid sulfur showed that the number of free radicals is about 10^{-5} mole/l. at 200°C. and increases by a factor of 100–200 between this temperature and 375°C. On the assumption that the sulfur polymer chains terminate in free radicals (an assumption which has been arrived at theoretically[107]), it appears from the paramagnetic data that the number-average degree of polymerization is roughly of the order of magnitude of 10^5.

From viscosity data,[104] the length of the flow segment in sulfur melts is found to be about 20 atoms; and the over-all weight-average chain length is roughly estimated at 1.2×10^4 sulfur atoms. It is interesting to note that the segment length obtained by applying the Eotvös equation to surface tension data on molten sulfur is 18 atoms. Treatment[109,110] of extrapolated elastic data on the quenched sulfur in terms of the theory[111] of high elasticity leads to a value of about 10^3–10^4 sulfur atoms in the average "free" chain segment between two fixed points in the elastic network (the so-called "lattice arc"). Since quenched sulfur free of additives flows very readily, the elastic data were obtained on sulfur containing varying amounts of phosphorus by extrapolating to zero phosphorus. These results, when taken together, indicate that the sulfur chains are firmly tangled together at about a hundred places along the length of an average chain which is made up of approximately a million sulfur atoms.

As shown in Figure 6-9, the viscosity-temperature curves of phosphorus-sulfur melts[94] appear to go through a maximum in the composition range from 0% to about 30% P, corresponding to a P/S mole ratio of 0–0.44. Up to a P/S mole ratio of about 0.35, there appears to be very little reduction in the viscosity of the phosphorus-sulfur melt. In the range where the P/S mole ratio increases from 0.35 to about 0.55, the viscosity maximum vanishes, so that it can be concluded that the long-chain polymers (with or without cross-linking) have practically disappeared, and that the liquid consists primarily of small molecular species, presumably the cage-like structures observed for the crystalline phosphorus sulfides. Unfortunately, because of the crystallization of P_4S_{10} and P_4S_7, it was not possible

[108] D. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **76**, 5891 (1954).

[109] H. Specker, *Angew. Chem.*, **65**, 299 (1953)

[110] H. Specker, *Kolloid-Z.*, **125**, 106 (1952); *Z. anorg. Chem.*, **261**, 116 (1950); J. A. Prins and J. Schenk, *Plastica*, **6**, 216 (1953).

[111] T. Alfrey, *Mechanical Behavior of High Polymers*, Interscience Publishers, Inc., New York, 1948, pp 234–337

to make viscosity measurements at the lower temperatures at which the viscosity maximum ought to appear for the phosphorus-sulfur melts, so that the conclusions drawn from the data are only approximate

As previously noted, the elastic properties of solidified $S\mu$ can be stabilized by the addition of a few per cent of phosphorus. In Figure 6-11 the elastic moduli of fibers made from quenched sulfur-phosphorus mixtures are shown as a function of the phosphorus content.[112] It should

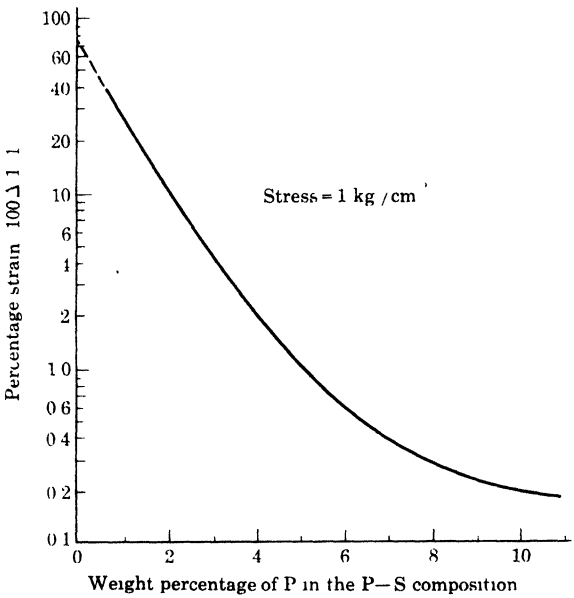


Fig. 6-11 The reversible deformation under a stress of 1 kg./cm.^{2} of elastic sulfur fibers containing phosphorus. Young's modulus in kg./cm.^{2} approximately equals 100/(percentage strain)

be noted that the modulus decreases quite rapidly with increasing phosphorus content. At the same time, the material becomes more brittle, and plastic flow is greatly reduced so that it appears that phosphorus "vulcanizes" the elastic sulfur in about the same way that sulfur vulcanizes rubber, *i.e.*, through crosslinking of the long chains. The vulcanizing effect of phosphorus is most readily observed in the reduction of plastic flow. Whereas sulfur quenched from a melt held at temperatures above

[112] J. C. Pernert, U. S. Pat. 2,577,207 (1951), Brit. Pat. 667,893 (1952, assigned to Oldbury Electrochem Co.).

160°C. is so plastic that it is virtually impossible to apply and remove a deforming force without obtaining permanent deformation, the addition of several per cent of phosphorus reduces the cold flow to inappreciably small values at such temperatures, so that in a normal experiment the deformation completely disappears when the deforming force is removed.

In Figure 6-12 the elastic (reversible) deformation under a stress of 1 kg./cm ^{2} is shown as a function of temperature for a number of sulfur-phosphorus mixtures The curves corresponding to 2% and 3% by weight of added phosphorus exhibit a plateau in which the elastic modulus

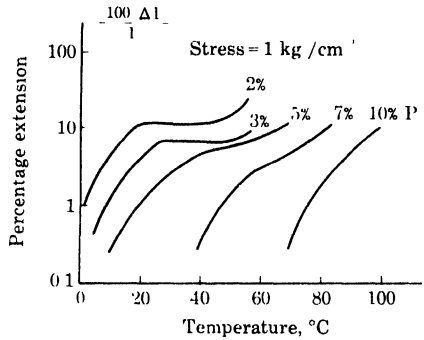


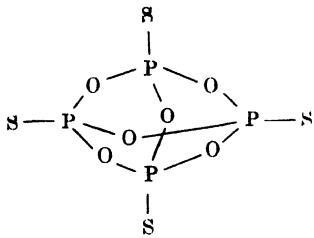
Fig 6-12 The deformation of sulfur fibers containing various amounts of phosphorus, as a function of temperature under a stress of 1 kg /cm ^{2}.

is roughly proportional to the absolute temperature, as demanded by the theory of high elasticity. The curve corresponding to 10% phosphorus represents virtually the end of the transition from an elastomeric to a vitreous type of system.

Phosphorus Oxysulfides

Four phosphorus oxysulfides have been described in the literature. They have the following empirical formulas: $P_2O_3S_2$, $P_2O_2S_3$, $P_4O_4S_3$, and $P_6O_{10}S_5$. The best characterized member of this group of compounds is the one with the empirical formula $P_2O_3S_2$. It has been made by mixing freshly distilled P_4O_6 with the calculated amount of sulfur in a sealed tube under a nitrogen atmosphere.[62] Upon heating, a violent reaction sets in when the temperature reaches 154–158°C. This product can also be made[110,89] by mixing three moles of P_2O_5 with two moles of P_2S_5. It is purified by sublimation. When sublimed in a vacuum at 140–150°C., the sublimate is in the form of hygroscopic, colorless, feathery crystals.

A number of different physical techniques have demonstrated that the compound with the empirical formula $P_2O_3S_2$ has a cage-like structure similar to that of P_4O_{10}, so that its true formula is $P_4O_6S_4$. An electron diffraction investigation[113] shows that the four sulfur atoms are in the isolated position, whereas the six oxygen atoms are in the bridging positions in the cage-like structure, the shape of which is shown below



POP = 123.5° ±1°
OPO = 101.5° ±1°
OPS = 116.5° ±1° (6-13)

As would be expected from the fact that the oxygen is in the bridging positions, the P-O distances of 1.61 ± 0.02 A. correspond to very little π-bond character, about 0.2 π-bond per σ-bond. However, the P-S distances of 1.85 ± 0.02 A correspond to considerable π-character because the sulfur atoms are in the isolated position. From the atom-center distances, it appears that the P-S bond exhibits about 1.0 π-bond per σ-bond.

The Raman spectrum has also been studied[114] and corresponds to a $P_4O_6S_4$ molecule, of symmetry T_d. The Raman results are in perfect accord with the electron diffraction data. Vapor density measurements indicate that the vapor is not decomposed at 400°C. or lower,[62] since the observed molecular weight was 343 as compared to the weight of 348 calculated for the formula $P_4O_6S_4$.

The phosphorus sulfoxide, $P_4O_6S_4$, melts at about 102°C. to a viscous liquid which boils at 295°C. The tetragonal crystals of $P_4O_6S_4$ are readily soluble in carbon disulfide. They can also be dissolved in benzene, but dissolution is accompanied by reaction resulting in the formation of dark-colored organic products. As previously stated, $P_4O_6S_4$ is hygroscopic and deliquescent. It dissolves rapidly in water, undergoing hydrolysis to give condensed phosphoric acids (presumably a thiotetrametaphosphoric acid is the major product) and hydrogen sulfide. In its properties, the phosphorus sulfoxide, $P_4O_6S_4$, resembles the H-form of phosphorus pentoxide, P_4O_{10}, more than it does phosphorus pentasulfide, P_4S_{10}.

[113] A. J. Stosick, *J. Am. Chem. Soc.*, **61**, 1130 (1939).

[114] H. Gerding and H. van Brederode, *Rec. trav. chim*, **64**, 183 (1945); *ibid.*, **67**, 677 (1948).

The compound with the empirical formula $P_2O_2S_3$ has been made by dissolving hydrogen sulfide in phosphorus oxychloride at 0°C. After recrystallization in additional phosphorus oxychloride at 150°C, a crystalline product with the formula $P_2O_2S_3$ is obtained.[115] When heated in a vacuum, the compound $P_2O_2S_3$ decomposes completely into phosphorus pentoxide and phosphorus pentasulfide. Presumably, this compound is made up of molecules having a cage-like structure, so that the true formula would be $P_4O_4S_6$. If there is but one kind of molecule, the sulfur atoms would probably be in the bridging positions in its structure.

The compound having the empirical formula $P_4S_3O_1$ is made[14] from reaction of the oxygen in air with P_4S_3. It is a yellowish powder, insoluble in ordinary solvents, having a melting point of 250°C. Presumably, this compound has a structure somewhat similar to that shown previously for P_4S_7. The phosphorus oxysulfide with the empirical formula $P_6O_{10}S_5$ is obtained[110] by redistillation of $P_4O_6S_4$ in the presence of excess P_4O_{10}. When purified by sublimation, this material appears as a hard, white, crystalline solid, melting at 122–125°C. As might be expected, this phosphorus oxysulfide is quite hygroscopic. It would seem that the $P_6O_{10}S_5$ is a mixed crystal equal to P_4O_{10} plus 5 $P_4O_6S_4$.

Tertiary Organic Phosphine Sulfides

The phosphine sulfides, R_3PS, are quite similar to the organic phosphine oxides, with respect to both methods of preparation and properties.[83] One of the best preparations is the direct reaction of sulfur with a tertiary phosphine. This reaction is ordinarily carried out in solution (ether, benzene, or carbon disulfide) on moderate warming. Because the reaction is usually rather exothermic and is accelerated by heating, it is common practice to add the sulfur gradually. Reaction is completed by refluxing.

In the preparation of organic phosphine sulfides, the sulfur also can be donated by an organic disulfide. Thus, triphenylphosphine is readily converted to the sulfide on warming with dibenzoyl disulfide, di-1-naphthyl disulfide, or dithiocarbamidodisulfide in toluene solution. It is interesting to note that dibenzyl disulfide is not effective. On prolonged standing or boiling in ether while exposed to the atmosphere, or by treatment with silver oxide, the adduct of triethylphosphine with carbon disulfide gives triethylphosphine sulfide. The same product also results from prolonged heating of triethylphosphine with ethyl mercaptan.

[115] A. Besson, *Compt. rend.*, **124**, 151 (1897).

As noted with the phosphine oxides, the melting points of the trialkylphosphine sulfides reach a minimum at the propyl or butyl derivative. Thus, trimethyl-, triethyl-, triisobutyl-, and triisoamylphosphine sulfides are crystalline compounds with the following melting points: 105°, 94°, 60°, and 96°C., respectively. Triphenylphosphine sulfide melts at about 160°C. The tertiary phosphine sulfides form adducts with alkyl halides such as methyl iodide. The adducts ionize in aqueous media and are very likely compounds of the sulfonium type. On being boiled in water they hydrolyze to give the tertiary phosphine oxide and an alkyl mercaptan, in which the alkyl group came from the alkyl halide.

Several phosphine sulfides in which all three of the organic radicals are different have been prepared, and one of these was optically resolved.[116] In order to effect this resolution, one of the organic radicals attached to the phosphorus contained a carboxylic acid group which was reacted with *d*-α-phenylethylamine hydrochloride. The optically active phosphine sulfide was phenyl-*p*-(carboxymethoxy)phenyl-*n*-butylphosphine sulfide, (4-[(HO)OCCH$_2$O]C$_6$H$_4$)P(C$_6$H$_5$)(C$_4$H$_9$)S The *d* and *l* forms of this acid exhibited the following optical rotations. $[M]$ = +9.6° and −9.7°, respectively

PHOSPHINE SELENIDES AND TELLURIDES

Phosphorus selenides with the following empirical formulas have been described[117,118] in the literature: P_2Se_5, P_2Se_3, and perhaps P_2Se, and P_4Se Of all of these, the P_2Se_5 is the best known It is made by heating a stoichiometric mixture of the elements. The resulting red-brown solid is dissolved in carbon tetrachloride by heating Upon being recrystallized from carbon tetrachloride, it is obtained as black needles. On heating, phosphorus pentaselenide decomposes to give phosphorus vapor and a residue of elemental selenium. Addition compounds with other selenides are known, *e.g.*, 2 CuSe·P_2Se_5 and 2 Ag_2Se·P_2Se_5.

Phosphorus triselenide is made by heating a stoichiometric mixture of the elements. This compound is a reddish colored solid which is insoluble in carbon disulfide. Like the pentaselenide, it also forms addition compounds with metal selenides -compounds such as 2 CuSe·P_2Se_3. Both

[116] W. C Davies and F. G Mann, *J. Chem. Soc*, **1944**, 276.

[117] R. Dubrisay, *Traité de Chimie Minerale*, ed P. Pascal, Masson, Paris, 1932, Vol. III.

[118] O. Hahn, *J. prakt. Chem.*, **93**, 430 (1864), B. Rathke, *Ann*, **152**, 181 (1869), W. Muthman and A. Clever, *Z anorg. Chem.*, **13**, 191 (1897), W Bogen, *Ann*, **124**, 57 (1862); J. Mai, *Ber.*, **61B**, 1807 (1928).

the tri- and pentaselenides are stable in dry air but slowly exchange oxygen for selenium in moist air by metathesis of the water vapor into hydrogen selenide.

Phosphorus tritelluride,[119] P_2Te_3, is made by heating powdered tellurium with white phosphorus in a sealed tube at 320°C. for an hour. It is a brittle black solid which cannot be dissolved in organic solvents or water Although stable in dry air, it decomposes very slowly in moist air to give off phosphine. Upon heating, P_2Te_3 does not melt but decomposes to phosphorus vapor and tellurium. It reacts with warm oxidizing agents. With a solution of iodine in carbon disulfide, it forms a precipitate having a composition equivalent to $P_2Te_3I_2$. This precipitate also forms when white phosphorus in carbon disulfide is reacted with TeI_2

UN-IONIZED PHOSPHORUS-NITROGEN COMPOUNDS

Preparation and Structure of Phosphonitrilic Chlorides[120]

Probably the best known compounds of phosphorus and nitrogen are the phosphonitrilic chlorides, which exhibit the empirical formula $PNCl_2$. These compounds are also known as phosphorus nitrilochlorides, phosphorus chloronitrides, or nitrilophosphoryl chlorides. Nearly all of the methods for preparation of the phosphonitrilic chlorides involve the partial ammonolysis of phosphorus pentachloride. In all cases, mixtures of the various polymers are obtained- mixtures which must be separated in order to obtain the individual members. The early workers[114] prepared phosphonitrilic chlorides in small yields by reacting gaseous ammonia with phosphorus pentachloride This preparative procedure was improved by Stokes[16] who used ammonium chloride as a source of ammonia, according to the following equation

$$x\,PCl_5 + x\,NH_4Cl \longrightarrow (PNCl_2)_x + 4x\,HCl \qquad (6\text{-}14)$$

The reaction shown in equation 6-14 was carried out in closed tubes between 150 and 200°C. Because of the formation of hydrogen chloride, high pressures were built up, so that the tubes had to be vented at frequent intervals. The resulting product consisted of a buttery mass containing some crystalline material. The trimer and tetramer were extracted from this mass with gasoline and fractionally recrystallized from anhydrous benzene. The pentamer, hexamer, and heptamer, together with an oily material having a composition and molecular weight corresponding to $(PNCl_2)_{11}$ were obtained from the gasoline mother liquor.

[119] E. Montignie, *Bull. soc. chim.*, **9**, 658 (1942).

Stokes' procedure also has been improved several times. According to the last modification of the method,[120] an intimate mixture of 52 g. of phosphorus pentachloride and 75 g. of ammonium chloride is placed in the bottom of a 50 cm. Pyrex tube having a diameter of 5 cm. The mixture is then covered to a depth of about 5 cm. with a capping of ammonium chloride. The tube, the outlet from which is connected to a wash bottle containing sulfuric acid, is immersed in an oil bath to such a depth that the ammonium chloride cap is kept largely above the liquid level. By heating for 4–6 hr. at a bath temperature of 145–160°C., it is found that 90–95% of the PCl_5 is converted into a mixture of phosphonitrilic chlorides. The end of the reaction is marked by practical cessation of the bubbling of hydrogen chloride through the sulfuric-acid trap. Extraction with low-boiling petroleum ether quantitatively removes the trimeric and tetrameric homologs which quite consistently occur to 38–43% of theory, based on the amount of phosphorus pentachloride used. The higher polymers are obtained from the residue by extraction with benzene, carbon tetrachloride, or chloroform. Evaporation of these extractions invariably results in the formation of thick, viscous oils or rubbery solids.

The reaction between phosphorus pentachloride and ammonium chloride can also be carried out in the presence of an inert solvent such as *sym.*-tetrachloroethane.[121] In this procedure 400 g. of PCl_5 and 125 g. of NH_4Cl are introduced into a liter of the solvent contained in a round-bottomed flask attached to a reflux condenser, to the outlet of which is fitted a calcium chloride tube, followed by an absorbent for HCl. Although the reaction is completed after 7 hr., it is found necessary to reflux the mixture for 20 hr. at 135°C. in order to drive off the dissolved HCl. After cooling, the excess NH_4Cl is removed by filtration. The buttery mass of phosphonitrilic chloride polymers is obtained by distilling off the solvent *in vacuo*. By washing the buttery mass with cold benzene, in which the trimer and tetramer are relatively insoluble, the higher polymers are removed. This leaves a partially purified mixture weighing about 100 g. and consisting of about three parts of trimer to one part of tetramer. After recrystallization from benzene, the trimer and tetramer are distilled at 10 mm. of Hg. At this pressure the trimer distills at 124°C. and the tetramer at 185°C. It should be noted that in addition to the use of solvent extraction and recrystallization for the purification and separation of the various phosphonitrilic chloride polymers, the trimer can also be separated from the other phosphonitrilic chlorides by steam distillation.

[120] L. F. Audrieth, R. Steinman, and A. D. F. Toy, *Chem. Revs.*, **32**, 109 (1943).
[121] R. Schenck and G. Romer, *Ber.*, **57B**, 1343 (1924).

However, if this is done, the chlorine atoms on the higher homologs are removed to a considerable extent by hydrolysis.

Vapor density measurements[122] on the trimer show that it has the formula $(PNCl_2)_3$. Likewise, the degree of polymerization of the tetramer was demonstrated by vapor density determinations and depression of the freezing point of benzene solutions.[16] The molecular weight of the pentamer, hexamer, and heptamer were obtained by Stokes[16] from the elevation of the boiling point of benzene solutions

The structure of trimeric phosphonitrilic chloride has been determined by electron diffraction.[123] This determination bears out the structure originally postulated by Stokes[16] in which there is a six-atom ring of alternating phosphorus and nitrogen atoms, with the two chlorine atoms being attached to the phosphorus. According to the diffraction work, the two nitrogen and two chlorine atoms surrounding the phosphorus form a distorted tetrahedra. However, the six-atom ring is flat, so that the nitrogen and phosphorus atoms lie in the same plane. The P-Cl distance is found to be 1.97 ± 0.03 A. and the P-N distance 1.65 ± 0.03 A. The Cl—P—Cl angle is 107-110° and $\angle NPN = \angle PNP = 120°$. The cyclic structure of the trimeric phosphonitrilic chloride is borne out by Raman measurements[124] which indicate that the symmetry of the molecule is D_{3h}.

X-ray diffraction analysis of crystals of the tetramer of phosphonitrilic chloride leads to similar results.[125] However, in this case the ring is not planar but is puckered, somewhat like the boat form of cyclohexane. In the $(PNCl_2)_4$ molecule, the P-N distance was found to be 1.68 A., the P-Cl distance 2.00 A., and the angles are: $\angle ClPCl = 106°$. It should be noted that there are four molecules in the unit cell of the trimer, the crystals of which belong to the rhombic system, and two molecules in the unit cell of the tetramer, the crystals of which are tetragonal.

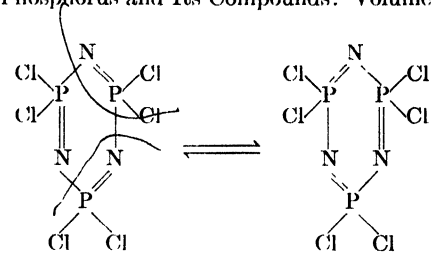
The planar ring found for the trimer has been interpreted to mean that the compound has essentially the same type of bonding as is exhibited by benzene. That is to say, there is alleged to be resonance between the two forms shown below:

[122] J. H. Gladstone and J. D. Holmes, *J. Chem. Soc.*, **17**, 225 (1864).

[123] L. O. Brockway and W. M. Bright, *J. Am. Chem. Soc.*, **65**, 1551 (1943).

[124] A. M. de Ficquelmont, M. Magat, and L. Ochs, *Compt. rend.*, **208**, 1900 (1939); J. V. Iribarne and D. G. de Kowalewski, *J. Chem. Phys.*, **20**, 346 (1952).

[125] J. A. A. Ketelaar and T. A. de Vries, *Rec. trav. chim.*, **58**, 1081 (1939); F. M Jaeger and J. Beintema, *Proc. Acad. Sci. Amsterdam*, **35**, 756 (1932).



(6-15)

However, the atom-center distances indicate only about 0.2 π-bond per σ-bond for P-N and about 0.1 π-bond per σ-bond for P-Cl for both the trimer with a planar ring and the tetramer with a puckered ring. Since the π-character of the bonds to the phosphorus involves this atom's outer *d*-orbitals, there is no reason that π-bonding should lead to a change in symmetry of its σ-bonds. This, of course, is not necessarily true for the nitrogen, in which the π-character of the bonding stems from use of the unshared pair of electrons. However, there is no *a priori* reason that the σ-bond structure accompanying π-bonding should lead to a planar ring.

Although no structure data are available, it is to be presumed that the higher crystalline homologs of the phosphonitrilic chlorides are also cyclic. However, the elastomeric or high-polymer form of $PNCl_2$ is presumably a linear chain.

High Polymers of Phosphonitrilic Chlorides

In addition to the compounds represented by the formulas $(PNCl_2)_x$, where x ranges from 3 to 7, there have been obtained (1) a higher molecular weight oil, found by Stokes to have an average composition represented by the formula $(PNCl_2)_{11}$; (2) gums; (3) waxes; (4) so-called "inorganic rubber," which is an elastomeric form of $PNCl_2$ having a very high degree of polymerization; and (5) an infusible, nonelastic material with an empirical formula still approximating $PNCl_2$. Presumably, the oil exhibiting the average composition $(PNCl_2)_{11}$ is primarily a mixture of ring homologs larger than the heptamer. The gums, waxes, and inorganic rubber are probably all chain polymers with some crosslinking. The infusible material is undoubtedly very greatly crosslinked.[126]

Stokes[16] was the first investigator to show that the crude mixture of phosphonitrilic chlorides is converted to a rubber-like material, slowly at

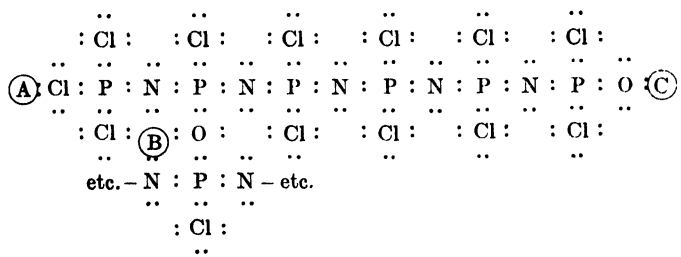
[126] For data on polymerization that is less definitive than that given in refs 121 and 127, see A. M. de Ficquelmont, *Compt. rend.*, **204**, 689, 867 (1937), and O. Schmitz-Dumont, *Z. Elektrochem.*, **45**, 651 (1939).

250°C. and very rapidly at 350°C. When the rubber-like mass was treated with benzene, lower polymers were extracted and finally the entire mass would swell and gelatinize. On evaporation of the benzene, the rubber-like substance was again obtained. The inorganic-rubber form of phosphonitrilic chloride absorbs a number of organic solvents as well as its lower molecular weight ring polymers. In dilute aqueous ammonia, the elastomer swells, gelatinizes, and then dissolves. The rubber-like form of $PNCl_2$ can be depolymerized at temperatures above 350°C., thereby distilling away to leave no residue if a purified sample is used.

The polymerization of the trimer and the tetramer has been studied,[127,121] both in bulk and in solution. In bulk polymerization most of the product is insoluble, with the amount of insoluble increasing at higher temperatures (in the range between 250 and 350°C.) and longer conversion periods. In this case, the soluble part exhibited a very low degree of polymerization of 3–7. Solution polymerization cannot be carried out in solvents containing hydrogen (*e.g.*, benzene, xylene, and hexane), since there is reaction with the solvent to give organophosphorus compounds plus hydrogen chloride. Chlorinated hydrocarbons, especially carbon tetrachloride, are suitable solvents for solution polymerization. Polymerization in solution gives considerably less insoluble material than does bulk polymerization, with degrees of polymerization up to 300 being reached in the soluble part. In both bulk and solution polymerization, the same results were obtained when $(PNCl_2)_3$ or $(PNCl_2)_4$ were used. Polymerization proceeds by a chain reaction in which oxygen plays an important role. Indeed, when oxygen is excluded, polymerization does not occur. In the presence of oxygen, the rate increases with O_2 concentration up to a limiting value at about 1% O_2 and then decreases slightly. Oxygen apparently initiates the polymerization by reacting with the trimer or tetramer ring, thereby breaking the ring and producing a radical. Oxygen apparently also plays the role of a chain terminator and a crosslinking agent. Polymerization–depolymerization equilibrium does not occur at lower temperatures; and the kinetic chain length has been calculated[127] to be up to 1000 times larger than that determined from the average degree of polymerization as would be expected in a mechanism involving chain transfer. The kinetic study by Patat and Kollinsky indicates that the polymerization of phosphonitrilic chlorides is of the normal type, often observed in organic polymer chemistry.

Some of the ways that oxygen can act as a chain terminator and crosslinking agent are shown in the following electronic structure picture:

[127] F. Patat and F. Kollinsky, *Makromol. Chem.*, **6**, 292 (1951).



(6-16)

In this representation the terminal chlorine at Ⓐ came from that part of the chain where the crosslinking oxygen, Ⓑ, now shares electrons with the phosphorus. The terminal oxygen, Ⓒ, at the other end of the chain takes the place of a nitrogen atom. According to the role which oxygen

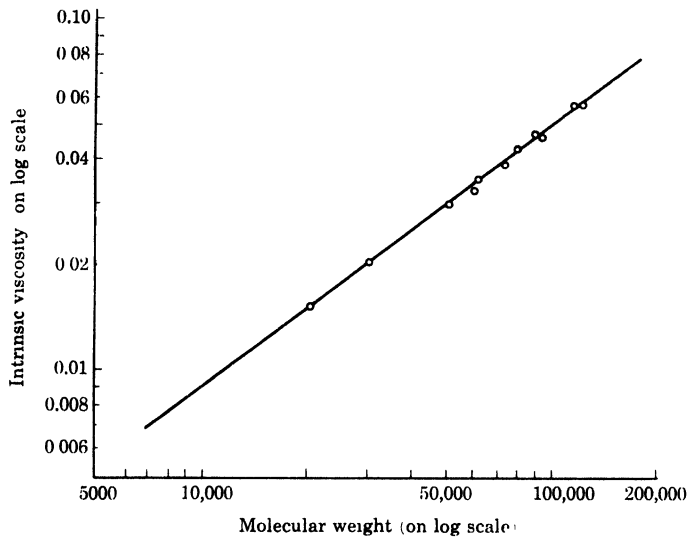


Fig. 6-13 Relationship of intrinsic viscosity (limiting viscosity number) with the molecular weight of polymeric phosphonitrilic chlorides. The molecular weight was obtained from limiting osmotic pressure data and both the viscosity and osmotic pressure measurements were carried out in the same solvent.

must play as a chain terminator, it is to be expected that scission of rings will lead to very long chains so that a partially polymerized mixture will consist of rings and long chains without much in the way of short chains—which, indeed, would have chemical compositions quite different from

$(PNCl_2)_x$. The same conclusion, that the chains must be long, is reached if end groups other than oxygen are assumed (even free-radical end groups).

The molecular weight of the polymerized phosphonitrilic chlorides can be obtained directly from osmotic-pressure measurements and indirectly from intrinsic viscosity. The experimentally determined relationship between the intrinsic viscosity and the number-average molecular weight,[127] obtained from osmotic pressure, is shown in Figure 6-13. Solubility fractionation of the polymers can be carried out from benzene solution by the stepwise addition of gasoline.

X-ray studies of the elastomeric form of phosphonitrilic chloride indicate that the unstretched material is amorphous but that, upon stretching, it crystallizes to give a fiber diagram.[128] This behavior is similar to that of rubber and other well-known organic elastomers. Theoretical interpretation of the fiber diagram indicates that there are long spiral chains having the configuration shown in Figure 6-14.

The amount of viscous flow in properly prepared fibers of elastomeric phosphonitrilic chlorides is very small, even when the fiber is extended by a factor of 2 or more. Thus the extension was found to be completely reversible,[109] within a small experimental error, when fibers were stretched to 199% of their original length under a stress of 1 kg./cm.^{2} applied for a minute. Such completely elastic behavior was observed throughout the wide temperature range of 50–160°C. For periods of extension longer than 75 sec. at 1 kg./cm.^{2}, the fibers did not shorten quite back to their original length, so that a small amount of viscous flow could be detected. However, at room temperature, the deformation is completely reversible even after a period of several hours at moderate extension.

It is interesting to note that phosphonitrilic chloride meets the requirements of an ideal elastomer, based on a stable molecular network, even better than slightly vulcanized, high-grade natural rubber. According to the theory of high elasticity,[111] the modulus of elasticity should be proportional to the absolute temperature. On one sample of elastomeric phosphonitrilic chloride, Young's modulus was found to be 2.5 kg./cm.^{2} at 313°K. and 3.2 kg./cm.^{2} at 413°K. Superimposed upon this behavior is the reversible crystallization within the structure. Thus, when the polymer is heated under constant deformation,[128] the stress increases to a degree which is more than proportional to the absolute temperature. On cooling, the tension remains at first higher than it was originally at the lower temperature and then finally decreases to the original value.

[128] K. H. Meyer, W. Lotmar, and G. W. Pankow, *Helv. Chim. Acta*, **19**, 930 (1936); also see M. L. Huggins, *J. Chem. Phys.*, **13**, 37 (1945).

This is attributed to (1) "melting" of the crystalline portions as the temperature is raised, with the molten portion then contributing to the stress, and (2) delayed crystallization on cooling. According to the theory of high elasticity, the tendency to contract is produced through thermal agitation of long segments of the flexible chain (the so-called, "lattice

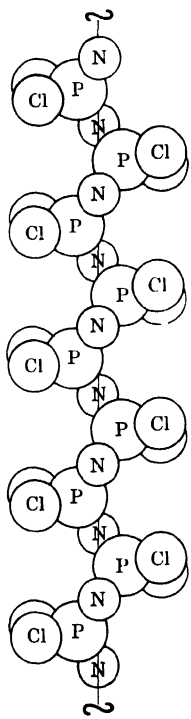
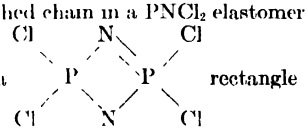


Fig. 6-14 A stretched chain in a $PNCl_2$ elastomer. The top view, down the axis of the chain, appears as a



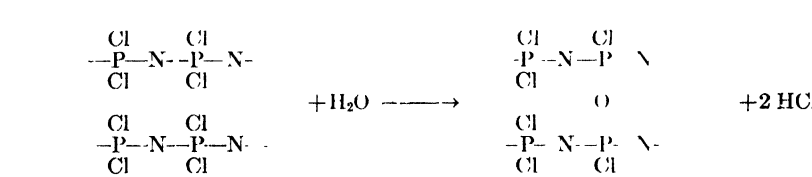
rectangle

ares") in the amorphous portions of the solid. The thermodynamically preferred condition is the relaxed state in which the chains are greatly disoriented and the solid is thus amorphous; instead of the stretched state corresponding to a portion of the chains being so well oriented as to be "crystallized."

From the average elastic modulus of 2 kg./cm.^{2} at 25°C., it is estimated[109]

that the average number of atoms lying between juncture points in the elastic network is approximately 10^3. This lattice-arc length is probably very many times less than the degree of polymerization of a $PNCl_2$ chain in inorganic rubber.

When highly elastic samples of inorganic rubber are stored in the absence of air, there is no change in their elastic properties. However, storage in air results in a considerable increase in the elastic modulus and in the brittleness of the samples, even after a few months. This is explained by the action of water in forming oxygen bridges from chain to chain so as to cause a considerable decrease in the average lattice arc length, with a concomitant increase in the modulus of elasticity [109]



(6-17)

As previously noted, much more extensive crosslinking of the polymer can be obtained by slowly heating it to a red heat in the presence of some air. In this case, the product is a porous, horny mass Presumably, the action of heat accelerates oxidation (with some hydrolysis as well) causing partial decomposition, which should also result in crosslinking.

Properties and Reactions of the Phosphonitrilic Chlorides

Some physical properties of the cyclic phosphonitrilic chlorides are given in Table 6-3 from which it can be seen that although the boiling points increase regularly as expected when going from the trimer to the heptamer, the melting points generally decrease with increasing molecular weight. Superimposed upon this decrease, there appears to be a saw-tooth variation in melting point, according to which the even-numbered polymers have higher melting points than the odd-numbered ones. Such a saw-tooth pattern of melting points has been observed for the homologous series of aliphatic acids. The decrease in melting point with increasing molecular weight for the phosphonitrilic chlorides is probably caused by poorer packing in the crystal lattice of the higher homologs as compared to the small ones It is interesting to note that the higher melting point of the tetramer (even-numbered polymer) as compared to the trimer is accompanied by a higher density.

The vapor pressures of several phosphonitrilic chlorides have been deter-

TABLE 6-3
Physical Properties of Some Cyclic Phosphonitrilic Chlorides

Formula	Specific gravity	Melting point (°C.)	Boiling points	
			At 13 mm (°C.)	At 760 mm (°C.)
$(PNCl_2)_3$	1 98	114	127	256
$(PNCl_2)_4$	2 18	123 5	188	328 5
$(PNCl_2)_5$	—	40 5–41	223–224 3	Polymerizes
$(PNCl_2)_6$		90–91	261–263	Polymerizes
$(PNCl_2)_7$	—	−18	289–294	Polymerizes

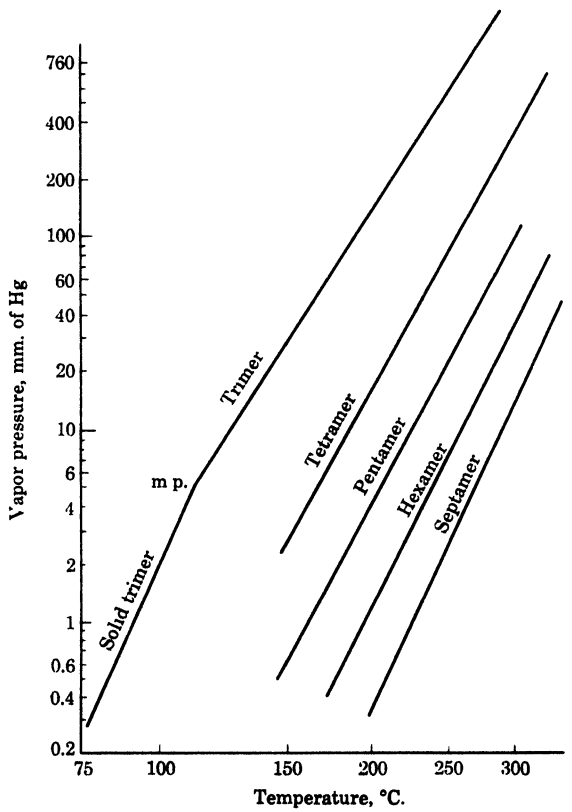


Fig. 6-15 Vapor pressure curves for various cyclic phosphonitrilic chlorides in liquid form All values are estimations except those for the trimer

mined and are shown in Figure 6-15.[129] The molar heat of vaporization for $(PNCl_2)_3$ is 13.2 kcal., and its molar heat of sublimation is 18.2 kcal. This means that the heat of fusion of trimeric phosphonitrilic chloride is 5.0 kcal., by difference. It should be noted that the trimeric and tetrameric forms of phosphonitrilic chloride exhibit a eutectic melting at 89°C. and corresponding to a trimer mole fraction around 0.65.[120]

Although few precise measurements of the solubility of the various polymers of phosphonitrilic chloride have been made, approximate solubility data are given in a number of places throughout this discussion. The available quantitative solubility data on the trimer and tetramer are presented in Table 6-4.

TABLE 6-4

Solubilities[120] of Trimeric and Tetrameric Phosphonitrilic Chlorides and the Trimeric Diamide

Solvent	Solubilities in g./100 g. of solvent at 20°C. of		
	$(PNCl_2)_3$	$(PNCl_2)_4$	$P_3N_3(NH_2)_2Cl_4$[a]
Ether	46 37	12 4	64 7
Dioxane	29 55	8 23	48 0
Benzene	55 0	21 42	1 55
Toluene	47 3	17 8	1 09
Xylene	38 85	13 85	0 73
Saturated petroleum hydrocarbons	27 9	8 39	0 09
Carbon tetrachloride	38.88	16 55	0.05
Carbon disulfide	52 05	22.00	0 13

[a] Values for $P_3N_3(NH_2)_2Cl_4$ are at 18°C.

In the terminology of the organic chemist, the phosphonitrilic chlorides are to be considered as acid chlorides, and the reactions which these substances undergo are quite similar to those of a relatively stable organic acid chloride. Mild hydrolysis leads to partially and completely hydroxylated products—the latter being known as the metaphosphimic acids (see Chapter 13). Vigorous hydrolysis can lead to intermediate orthophosphamidic acids, with an equimolar mixture of phosphoric acid and ammonium chloride as the final products of hydrolysis. The over-all empirical equation showing one intermediate step in the process is given below.

[129] R. Steinman, F. B. Schirmer, Jr., and L. F. Audrieth, *J. Am. Chem. Soc.*, **64**, 2377 (1942); H. Moureu and A. M. de Ficquelmont, *Compt. rend.*, **213**, 306 (1941).

$$(PNCl_2)_x + 4x\ H_2O \longrightarrow (PNHO_2)_x^{x-} + 2x\ Cl^- + 3x\ H^+ + 2x\ H_2O \longrightarrow$$
$$x HPO_4^{2-} + 2x\ Cl^- + 3x\ H^+ + x\ NH_4^+ \quad (6\text{-}18)$$

Since the phosphonitrilic chlorides are insoluble in water, the rate of hydrolysis can be greatly increased by dissolving the phosphonitrilic chloride in a solvent, such as ether, which is then shaken with water. From the hydrolysis of $(PNCl_2)_3$, the acid $P_3N_3Cl_4(OH)_2$, and derivatives of $[PN(OH)_2]_3$ have been obtained in crystalline form.[120] The compound $[PN(OH)_2]_4 \cdot 2\ H_2O$ is a very stable crystalline compound which is formed by the action of water on solutions of the tetramer in ether. When steam distillation is used to volatilize trimeric phosphonitrilic chloride from the tetramer, the latter hydrolyzes rapidly to give this slightly soluble acid, $[PN(OH)_2]_4 \cdot 2\ H_2O$. When solutions of the trimeric and tetrameric phosphonitrilic chlorides in pyridine are treated with water, products are obtained which contain no halogen and exhibit the analysis expected for the pyridine salts of metaphosphimic acids.[121] These products lose pyridine rapidly when held in a vacuum over sulfuric acid or when heated under reduced pressure, thereby yielding hygroscopic powders which dissolve in water to give acidic solutions. These solutions coagulate albumen, indicating that the anions contained therein have quite a large molecular weight. When solutions of the higher phosphonitrilic chlorides (including inorganic rubber) in ether are shaken with aqueous alkaline solutions, hydrolysis is rapid. Presumably, the products are salts of high molecular weight phosphonitrilic acids.

As might be expected, ammonia acts quite similarly to water in its reactions with the phosphonitrilic chlorides. Thus, a crystalline product with the formula $P_3N_3(NH_2)_2Cl_4$ is obtained by the action of aqueous or gaseous ammonia upon a solution of $(PNCl_2)_3$ in ether. The solubilities of this compound are shown in Table 6-4. The melting point of this tri(phosphonitrile)diamidotetrachloride is 162°C., and some decomposition occurs upon melting. Hydrogen chloride is lost from the compound when it is heated in a vacuum at 170°C. However, even at 600°C., all of the chlorine is not removed. If the compound is heated in a current of ammonia at 800–825°C., conversion to the nitride, P_3N_5, is finally effected.

With respect to the problem of the ammonolysis of phosphorus pentachloride, it is interesting to note that a small quantity of $P_3N_3(NH_2)_2Cl_4$ has been obtained[130] as a byproduct in the treatment of a cold solution of phosphorus pentachloride in carbon tetrachloride with gaseous ammonia. While most of the pentachloride reacted to form a precipitate, a small

[130] H. Moureu and P. Rocquet, *Bull. soc. chim. France*, **3**, 821 (1936).

quantity of $P_3N_3(NH_2)_2Cl_4$ remained dissolved in the carbon tetrachloride.

By extended reaction (several months) between liquid ammonia and trimeric phosphonitrilic chloride in a sealed tube, a product having the empirical composition PN_3H is obtained.[120] This product can be formulated as $[PN(NH_2)_2]_3$. It is very soluble in water but can be precipitated as a monohydrate by the addition of alcohol to the aqueous solution. When heated in a vacuum for several days at 200°C., the compound loses ammonia, and the residue gradually approaches the empirical composition PN_2H corresponding to phospham. It should be noted that when gaseous ammonia is passed over molten trimeric phosphonitrilic chloride, the latter is converted into a greyish white infusible powder having a composition approaching that of phospham, PN_2H, with a few per cent of residual chlorine.

Amines react with the phosphonitrilic chlorides in about the same way as ammonia reacts. Thus, the reaction shown below for the case of the trimeric phosphonitrilic chloride has been found to hold when either the trimer or the tetramer is allowed to react with such amines as *p*- or *o*-toluidine, aniline, and piperidine, as well as with phenylhydrazine.[120]

$$(PNCl_2)_n + 12\,RNH_2 \longrightarrow [PN(NHR)_2]_3 + 6\,RNH_2HCl \qquad (6\text{-}19)$$

Since molecular weight determinations show that the products obtained from trimeric phosphonitrilic chloride are different from those derived from the tetramer, it appears that no depolymerization is involved in this reaction. In Table 6-5 the formulas and melting points for a number of products made according to the reaction shown in equation 6-19 are presented. These products can be called *N*-substituted phosphonitrilamides. Esters of amino acids have also been reacted with phosphonitrilic

TABLE 6-5
Reaction Products of Cyclic Phosphonitrilic Chlorides with Organic Amines

Formula of the *N*-substituted phosphonitrilamide	Amine	Melting point (°C.)
$[PN(NHC_6H_4\cdot CH_3)_2]_3$	*p*-Toluidine	243
$[PN(NHC_6H_4\cdot CH_3)_2]_3$	*o*-Toluidine	241–2
$[PN(NHC_6H_5)_2]_3$	Aniline	268 (267)
$[PN(NHC_5H_{10})_2]_3$	Piperidine	231
$[PN(NH\cdot NHC_6H_5)_2]_3$	Phenylhydrazine	200
$[PN(NHC_6H_5)_2]_4$	Aniline	244

chlorides according to equation 6-17.[131] In the case of the trimeric phosphonitrilic chloride, only two of the six chlorine atoms are replaced. The products from the reactions with amino acid esters are recovered as oils. In the case of these reaction products with the tetrameric phosphonitrilic chloride, treatment of the oils with acetone leads to crystalline acetone addition products.

Adducts of the phosphonitrilic chlorides with tertiary amines have also been reported in the literature.[120] In view of the fact that the addition compounds obtained from the trimeric and tetrameric phosphonitrilic chloride exhibited the same melting points, the assumption has been made[131] that the ring structures of the phosphonitrilic chlorides are degraded during reaction, so that the adducts correspond to the simple monomer: $PNCl_2 \cdot 2\,NR_3$.

Regardless of their structure, it should be noted that solutions of trimeric or tetrameric phosphonitrilic chlorides in pyridine are extraordinarily reactive. Clear solutions are obtained in the absence of moisture. Since a trace of water immediately gives a cloudy precipitate, the phosphonitrilic chlorides have been suggested for drying pyridine. The use of pyridine as a solvent for reacting phosphonitrilic chlorides with alcohols has been investigated. From this reaction, polymeric phosphonitrilic esters—a new type of organic-inorganic plastic—have been made.[132] These materials have been characterized from the viewpoint of the polymer chemist.

Although the reactions of the phosphonitrilic chlorides with alcohols and phenols have been the subject of considerable study,[120] no ester of the metaphosphimic acids presumably produced by these reactions has been positively identified and characterized. The reaction of trimeric phosphonitrilic chloride with absolute methanol is quite typical. At first, appreciable quantities of methyl chloride are evolved, the mixture then becomes turbid, and hydrogen chloride starts to come off. Long heating leads to the separation of a crystalline product which, after washing with methyl alcohol, ether, and drying, is shown by analysis to have the empirical composition, $PNOH(OCH_3)$. In forming an empirical formula weight of this product, approximately a mole of methyl chloride and a mole of hydrogen chloride were produced. When tetrameric phosphonitrilic chloride is used, the product corresponds to somewhat greater esterification. The reaction product with ethyl alcohol has the empirical

[131] H. Schäperkötter, "Über die Einwirkung von Tertiaren Aminen, Aminosaureestern und Ammoniak auf Phosphonitrilchloride," Dissertation, Westfälischen Wilhelms-Universitat zu Münster i. Westf., 1925.

[132] F. Goldschmidt and B. R. Dishon, *J. Polymer Sci.*, **3**, 481 (1948).

formula $O[PN(OC_2H_5)_2]_2$. A number of other alcohols give reaction products having approximately the same empirical formula. Probably the most reliable preparation of an organic derivative of a metaphosphimic acid results from reaction of the silver salt of the acid, $Ag_3(PO_2NH)_3$, with ethyl iodide.[133] In this case, the expected ester is not produced, since the ethyl group is thought to attach to the nitrogen atom.

The phosphonitrilic chlorides form 1:1 addition compounds with phosphorus oxychloride and phosphorus pentachloride,[134] Molecular weight determinations show that the $POCl_3 \cdot PNCl_2$ addition compound is based on monomeric $PNCl_2$. The infrared spectrum of this addition compound is very similar to that of pure $POCl_3$. It has been interpreted to show a chlorine bond between the two phosphorus atoms, corresponding to the structure: (O) $Cl_2PClPCl_2$(N). A more reasonable structure, however, is (O)Cl_2PNPCl_3. Both structures are in accord with the nuclear magnetic resonance spectrum which only shows the presence of two different kinds of phosphorus connected through an intermediate atom in the structure.

The reaction between the various phosphonitrilic chlorides and hydrocarbons, such as hexane or benzene, which occurs on heating[127] or under the effect of ultraviolet light[135] is at least superficially similar to the oxidative phosphonation of hydrocarbons described on p. 232, since in both cases a hydrogen on a hydrocarbon is readily replaced by a phosphorus atom, to which a chlorine as well as an oxygen or nitrogen atom is attached. In the case of the phosphonitrilic chlorides, both aliphatic and aromatic hydrocarbons react to give continuing successive substitution of the chlorines in the PNCl molecule by the aliphatic or aromatic radicals. Benzene gives phenyl derivatives of the phosphonitrilic chloride and hexane leads to hexyl derivatives.

Relatively unstable addition compounds are formed between trimeric phosphonitrilic chloride and sulfur dioxide or nitrogen dioxide.[136,137]

Other Phosphonitrilic Halides

Phosphonitrilic bromides having the formulas $(PNBr_2)_3$ and $(PNBr_2)_n$ are also known. In their preparation, which parallels that of the chlorides, phosphorus pentabromide is treated with ammonia or ammonium bro-

[133] R. Rätz and M. Hess, *Chem. Ber.*, **84**, 889 (1951).

[134] G. Barth-Wehrenalp, private communication from the Pennsylvania Salt Manufacturing Co.

[135] B. R. Dishon and Y. Hirshberg, *J. Polymer Sci.*, **4**, 75 (1949).

[136] M. Goehring, H. Hohenschutz, and R. Appel, *Z. Naturforsch.*, **9B**, 678 (1954).

[137] A. Besson and G. Rosset, *Compt. rend.*, **143**, 37 (1906).

mide.[137] Substitution of part of the chlorine in $(PNCl_2)_3$ by fluorine has been accomplished[138] by heating a mixture of $(PNCl_2)_3$ and PbF_2 in an atmosphere of nitrogen at 130–180°C. After distillation, a product having a peculiar odor resembling that of hydrogen cyanide is obtained. It has the formula $P_4N_4Cl_2F_6$, according to chemical analysis and molecular weight determinations. In addition to this product, another one having a composition corresponding to the formula $P_4N_4Cl_4F_4$ also results. Upon heating either of these compounds, an elastomer is obtained. The elastomeric product obtained from $P_4N_4Cl_4F_4$ can be decomposed at 400°C. to give two liquid fractions which are believed to have the following formulas: $P_3N_3Cl_2F_4$ and $P_3N_3Cl_4F_2$.

Phosphorus Amides

Aside from the literature written before 1900,[60] there have only been a few papers[130,139–141] on the amides of phosphorus. When ammonia is blown into a cold solution of a phosphorus halide in a neutral solvent such as carbon tetrachloride, a precipitate is produced in which there is approximately two moles of ammonia for each mole of halogen in the phosphorus halide. There is considerable evidence that this precipitate contains an appreciable proportion of ammonium halide, and therefore the following equation has been postulated by Perpérot for the reaction.[139]

$$PX_n + 2n\,NH_3 \longrightarrow P(NH_2)_n + n\,NH_4X \qquad (6\text{-}20)$$

where $n = 3$ or 5

Because the solubility of the phosphorus amides is very similar to that of the ammonium halides in solvents in which the phosphorus amides are not decomposed, the problem of separating the products of the reaction between the phosphorus halides and ammonia is extremely difficult. Therefore, the majority of investigators have had to study the phosphorus amides contaminated with more or less ammonium halide.

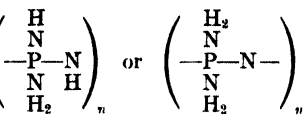
The existence of a triamide, $P(NH_2)_3$, seems reasonable, but the postulated pentamide, $P(NH_2)_5$, most probably has never been made. In its place Moureu and Rocquet claimed to have found a diiminoamide, with

[138] O. Schmitz-Dumont and H. Kulkens, *Z. anorg. u. allgem. Chem.*, **238**, 189 (1938); O. Schmitz-Dumont and A. Braschos, *ibid.*, **243**, 118 (1940).

[139] H. Moureu and P. Rocquet, *Compt. rend.*, **197**, 1643 (1933); G. Perpérot, *ibid.*, **181**, 662 (1925); C. Hugot, *ibid.*, **141**, 1235 (1905); A. Joannis, *ibid.*, **139**, 364 (1904).

[140] R. Klement and O. Koch, *Chem. Ber.*, **87**, 333 (1954); R. Klement and L. Benek, *Z. anorg. u. allgem. Chem.*, **287**, 12 (1956).

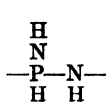
[141] M. Goehring and K. Niedenzu, *Chem. Ber.*, **89**, 1768, 1771, 1774 (1956), *ibid.*, **90**, 151 (1957).



(6-21)

the empirical formula $(HN)_2PNH_2$. Although there is no experimental evidence as to the structure of this material, it is quite probably not a compound based on one phosphorus atom but may consist of chains of units. Formation of such a compound would correspond to the reaction of 8 moles of ammonia with 1 mole of phosphorus pentachloride instead of the 10 moles required by equation 6-20. It should be noted that the experimental results of Perpérot[139] corresponded to about 9.5 moles of ammonia. As an alternative to the formation of a compound having the approximate composition $(HN)_2PNH_2$, it is possible that the reaction product between phosphorus pentachloride and ammonia is a complex mixture or even a complicated, three-dimensional P—N—H polymer of indefinite composition.

Phosphorus triamide and the postulated phosphorus iminoamide must be formed at low temperatures. Although a solvent has usually been used in their preparation, it is also possible to react ammonia and the phosphorus halides together in pure form to get reaction products which presumably contain a mixture of substances. Thus, phosphorus halides can be added to liquid ammonia, or ammonia vapor can be passed over the phosphorus halides. When the temperature is reasonably high (above about 0°C. according to some of the literature), there is some loss of nitrogen so that more condensed products than the amides are formed. Thus, at 0°C. the compound $P(NH_2)_3$ is supposed to decompose into a material having the empirical formula $P_2N_3H_3 \approx P_2(NH)_3$, which has been called phosphorus triimide. Another composition with the empirical formula PN_2H_3 is said to be formed by passing phosphorus trichloride vapor in a current of dry nitrogen through liquid ammonia at −78°C. This material has quite arbitrarily been called "imidophosphamide" on the basis of the hypothetical formula $HNPNH_2$. Obviously, this is an absurd formulation, since it indicates that phosphorus is present as a hybrid lying somewhere between p^2 and sp. If there is a single compound having the empirical formula PN_2H_3, a possible structure for it would be rings or long chains made up of



units. As the entire field is in a state of extreme confusion at present, the reaction products obtained by combining the phosphorus tri- and pentahalides with ammonia under various conditions should be very carefully reinvestigated using modern physicochemical techniques, especially x-ray diffraction.

Thanks to two recent papers by Klement,[140] a reasonably clear picture of the chemistry of the phosphoryl amides is now available. The triamide of orthophosphoric acid, $OP(NH_2)_3$ is prepared[140] by dropwise addition of a cooled solution of phosphoryl chloride in chloroform to a well-stirred solution of ammonia in the same solvent at $-10°C.$, so that the following reaction proceeded.

$$POCl_3 + 6\,NH_3 = OP(NH_2)_3 + 3\,NH_4Cl \qquad (6\text{-}22)$$

Isolation of the orthophosphoryl triamide is very difficult, because it has approximately the same solubility characteristics as ammonium chloride. However, pure $OP(NH_2)_3$ has been obtained by addition of diethyl amine to the reaction products suspended in chloroform. The diethyl amine reacts with the ammonium chloride to give free ammonia plus diethylammonium chloride, which is soluble in the chloroform. The remaining, nearly halogen-free orthophosphoryl triamide is then washed with chloroform, vacuum dried, and purified by recrystallization from absolute methanol. It appears in the form of colorless needles which are only slightly soluble in water. This compound is insoluble in chloroform, ethyl alcohol, ether, acetone, nitrobenzene, and pyridine. About 0.7 g. can be dissolved in 100 cc. of absolute methanol at 20°C. Molecular weight measurements in water agree with the simple formula $OP(NH_2)_3$. As expected, the compound is not appreciably ionized in water, since the specific conductivity of a 0.1 *M* solution at 20°C. is 10^{-4} mhos/cm., and the solution is essentially neutral (pH = 6).

Orthophosphoryl triamide is stable in dry air, but it loses ammonia after being exposed for about a month in moist air to form monoammonium phosphoramidate, $NH_4HPO_3(NH_2)$. When warmed with dilute sodium hydroxide, the orthophosphoryl amide forms sodium phosphorodiamidate, $NaPO_2(NH_2)_2$ plus ammonia. Since it is an acid amide, $OP(NH_2)_3$ can form complexes somewhat similar to those of urea. Thus, the following complexes with silver nitrate and with mercuric nitrate have been described:[140] $[OP(NH_2)_3]AgNO_3$ and $Hg_5[OP(NH)_3]_2(NO_3)_4$. Presumably, the amido (or imido) groups are coordinated with the metal ions in complexes of this type.

When ammonia and orthophosphoryl chloride are combined at elevated temperatures, about 150–200°C., an insoluble product is formed from which the ammonium chloride can easily be removed by washing with water. In this case, there are about two moles of nitrogen to one of phosphorus in the product, which is presumably a three-dimensional polymer. Heating of either this product or orthophosphoryl triamide causes continued loss of ammonia, with more and more condensation, until a composition roughly approximating PNO is reached.

By combining thiophosphoryl chloride with ammonia in the same manner that phosphoryl chloride was reacted with ammonia, the orthothiophosphoryl triamide, $SP(NH_2)_3$, is obtained.[140] After purification in the same manner that the orthophosphoryl triamide was purified, colorless crystals are obtained which are also only slightly soluble in water. The solubility of $SP(NH_2)_3$ in absolute methanol is approximately three times larger than that of $OP(NH_2)_3$. The action of moist air produces in this case (after about four weeks at room temperature) diammonium monothiophosphate, $(NH_4)_2HPO_3S$ Warming with dilute sodium hydroxide leads to sodium thiophosphorodiamidate, $NaPOS(NH_2)_2$, and ammonia. As might be expected, heating orthothiophosphoryl triamide with dilute acid causes release of hydrogen sulfide, as is the case with other thiophosphoryl compounds. Heating in a vacuum causes loss of nitrogen, sulfur, and hydrogen to give an impure phosphorus nitride, P_3N_5, at temperatures around 800°C.

When pyrophosphoryl chloride dissolved in chloroform is treated with anhydrous ammonia at 0°C., pyrophosphoryl amide, $(H_2N)_2OPOPO(NH_2)_2$, is formed.[141] The equation for the reaction is given below.

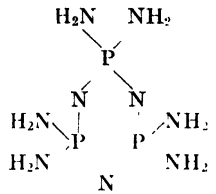
$$\begin{matrix} O & O \\ ClP—O—PCl \\ Cl & Cl \end{matrix} + 8\,NH_3 \longrightarrow \begin{matrix} O & O \\ H_2NP—O—PNH_2 \\ N & N \\ H_2 & H_2 \end{matrix} + 4\,NH_4Cl \qquad (6\text{-}23)$$

Isolation of the pyrophosphoryl amide is best carried out by extracting the ammonium chloride with liquid ammonia in which the amide is only slightly soluble.

Like the ortho compound, pyrophosphoryl amide is stable in dry air. In moist air it slowly undergoes hydrolysis to form diammonium pyrophosphoro-1,2-diamidate according to the following equation.

$$\begin{matrix} O & O \\ H_2NP—O—PNH_2 \\ N & N \\ H_2 & H_2 \end{matrix} + 2\,H_2O \longrightarrow \begin{matrix} O & O \\ H_2NP—O—PNH_2 \\ —O & O— \end{matrix} + 2\,NH_4^+ \qquad (6\text{-}24)$$

As previously noted, trimeric phosphonitrilic chloride can be reacted with liquid ammonia in a sealed tube for a long period of time (1 to 2 months) in such a way that the phosphorus compound is completely ammonated.[143] Since the resulting amide is completely insoluble in liquid ammonia, whereas ammonium chloride is soluble, decanting the ammonia gives a product, the composition of which corresponds to the empirical formula PN_3H_4 or $PN(NH_2)_2$. The product is very soluble in water but can be precipitated[130] as a monohydrate, $[PN(NH_2)_2]_3 \cdot H_2O$, by addition of alcohol to its aqueous solution. The formula of this compound is believed to be the following



(6-25)

An alleged new compound,[142] supposed to have the empirical formula PNO_2H_2, could be considered as a cyclic amide. However, recent work at Monsanto has shown that this compound is simply monoammonium orthophosphate.

Solid Phosphorus Nitrides and Some Related Compounds

As is the case with the amides of phosphorus, the available information on the phosphorus nitrides is very confused and needs considerable reinterpretation in order to be understood. In the early literature[60,117] solid materials exhibiting the empirical formulas PN and P_3N_5 have been described. In addition, a material having the empirical formula P_2N_3 appears in the more recent literature.[144] The most comprehensive studies have been carried out by Moureu, Wetroff, and Rocquet[144,145] in France and by the TVA laboratories[146] in the United States. According to the data obtained

[142] P. Renaud, *Compt. rend.*, **198,** 1159 (1934), *Ann. chim.*, **3,** 443 (1935).

[143] A. Besson and G. Rosset, *Compt. rend.*, **146,** 1149 (1908).

[144] H. Moureu and G. Wetroff, *Compt. rend.*, **201,** 1381 (1935); *Bull. soc. chim. France,* **4,** 918 (1937).

[145] H. Moureu and P. Rocquet, *Bull. soc. chim. France,* **3,** 1801 (1936); *Compt. rend.,* **198,** 1691 (1934); H. Moureu, B. Rosen, and G. Wetroff, *ibid.,* **209,** 207 (1939); H. Moureu and G. Wetroff, *Bull. soc. chim. France,* **4,** 1839 (1937); *Compt. rend.,* **207,** 915 (1938); G. Wetroff, *ibid.,* **208,** 580 (1939).

[146] E. O. Huffman, G. Tarbutton, K. L. Elmore, W. E. Cate, H. K. Walters, and G. V. Elmore, *J. Am. Chem. Soc.,* **76,** 6239 (1954); E. O. Huffman, G. Tarbutton, G. V. Elmore, A. J. Smith, H. K. Walters, M. S. Rountree, *J. Am. Chem. Soc.,* **79,** 1769 (1957); also unpublished work from the TVA laboratories at Wilson Dam, Alabama.

by these authors, there appears to be a series of amorphous phosphorus nitrides having N/P mole ratios ranging from about 0.9 to values as high as 1.7. In addition, one crystalline phosphorus nitride having the empirical formula P_3N_5 has been obtained.[146]

The amorphous phosphorus nitrides having N/P mole ratios between 1 and 1.5 are most readily prepared by passing a current of phosphorus vapor in nitrogen through an electric arc run at several thousand volts between tungsten electrodes. This is a hot arc, with the total gas pressure being approximately 1 atm. By heating phosphorus nitrides made in this fashion (so as to exhibit relatively low N/P mole ratios) in a current of ammonia at temperatures in the range of 800–900°C., the N/P mole ratio is raised up to about 1.7, *i.e.*, a ratio corresponding approximately to the empirical formula P_3N_5. By heating the reaction product of phosphorus pentachloride and ammonia in a furnace in which the temperature is raised over a period of about eight hours to 850°C., with a current of dry ammonia being maintained throughout the process, a nitride with an N/P ratio around 1.7 is also obtained.[147] Nitrides with this same composition can be made[145] by heating phospham, PN_2H, in a vacuum at temperatures between 450–720°C. Phosphorus nitrides are also prepared by direct synthesis from the elements in the presence of a heated tungsten filament.[146] A silent electrical discharge can also be employed to synthesize the phosphorus nitrides.[148]

The hot-wire synthesis of the solid phosphorus nitrides has been investigated as a rate process.[146] The apparent activation energy for the homogeneous synthesis of the gaseous PN molecule is about 31 kcal./mole; but synthesis of the solid material of this composition, as catalyzed by a hot tungsten surface, corresponds to an activation energy of 58 kcal./g. empirical formula weight. The mechanism of the process appears to be that the phosphorus atoms produced at the tungsten surface from P_4 and/or P_2 molecules react with nitrogen molecules to form the complex PNN, which further reacts with another phosphorus atom. The resulting groupings then probably combine to yield the polymer $(PN)_n$, or they may continue to grow through alternate collisions with nitrogen molecules and phosphorus atoms to give an N/P mole ratio as great as 1.7. At temperatures above 450°C. there is a spectroscopically detectable amount of gaseous PN, as well as elemental phosphorus and nitrogen over solid PN.

As prepared, the phosphorus nitrides range in color from white through

[147] A. Stock and H. Grüneberg, *Ber.*, **40**, 2573 (1907)

[148] V. P. Postnikov and L. L. Kuz'min, *J. Appl. Chem.* (*U.S.S.R.*), **8**, 429 (1935); W. Moldenhauer and H. Dorsam, *Ber.*, **59B**, 926 (1926); G. S. Deshmukh and Y. D. Kane, *Proc. Indian Acad. Sci.*, **25A**, 247 (1947).

yellow or tan to dark brown. Presumably, the pure phosphorus nitrides are white, with the dark coloration perhaps coming from admixed red phosphorus or from nitrides very high in phosphorus. Very often in the preparation of phosphorus nitrides, layers exhibiting different N/P ratios and different colors are produced. This is no indication that solid amorphous phosphorus nitrides exhibit fixed formulas such as PN, P_2N_3, and P_3N_5, even though the various layers may exhibit N/P ratios quite close to the whole-number fractions corresponding to these fomulas.

Completely amorphous phosphorus nitrides are known for N/P mole ratios ranging from 0.9 to 1.7. These materials all give off gaseous PN when heated in a vacuum, so that an amorphous substance for which the N/P ratio is about 1.0 will distill to leave no solid residue. An intermediate amorphous phosphorus nitride having an N/P ratio of, say, 1.2 will lose PN and leave a residue with an N/P mole ratio of about 1.7. With stronger heating, the latter material then gives gaseous PN and nitrogen. The gaseous PN can be condensed as such, but it will not react with gaseous nitrogen to form materials with an N/P ratio much higher than unity unless there is an electrical discharge or catalyst to give dissocation of the N_2 molecules.

Solid phosphorus nitrides for which the N/P mole ratio is in the neighborhood of 1.6–1.7 crystallize quite readily at temperatures around 750°C. This crystalline product is in the form of subhedral, acicular rosettes or clusters of subhedral rods. It exhibits sharp powder x-ray diffraction patterns. Although a structure analysis has not been carried out, the crystal is presumably some type of a high-polymer network, either planar or three-dimensional.

At room temperature the phosphorus nitrides are quite inert. Cold water has little action upon them and hot water reacts inappreciably slowly under most experimental conditions. Cold aqueous solutions of all kinds, including concentrated nitric acid have no action. This is also true for other strong chemical agents such as chlorine vapor. However, the phosphorus nitrides begin to act as powerful reducing agents when heated to temperatures above about 500–700°C. This action at high temperatures may be attributed to dissociation of the nitrides to give nitrogen and elemental phosphorus.

When P_3N_5 is heated with powdered magnesium up to temperatures around 810°C., a product with the empirical composition PN_3Mg is formed along with magnesium phosphide.[149] This product is a yellowish crystalline powder which is resistant to chemical action at room temperature. It is

[149] H. Moureu and G. Wetroff, *Compt. rend.*, **210**, 436 (1940).

quite possible that this material is a mixed phosphide-nitride of magnesium. Indeed, when calcium is used in place of magnesium, the resulting product cannot be separated from the calcium phosphide, Ca_3P_2. It is interesting to note that several thermodynamic studies have been carried out on the heats of formation of the phosphorus nitrides.[150]

Investigations at the TVA laboratories indicate that, at the same temperature, the amorphous phosphorus nitrides with low N/P ratios hydrolyze slower than do the amorphous phosphorus nitrides with higher ratios.[146] The activation energy for the hydrolysis of the nitride for which N/P equals 1.65 was found to be about 30 kcal./mole. Under steam pressure at 150°C., the hydrolysis half life for this material was found to be 55 hr.

Another very inert material with the approximate formula PN_2H has been described a number of times in the literature under the name phospham.[117] It has been made by heating the products formed by reacting ammonia with various phosphorus halides. It is described as an infusible white powder which is very stable in air and insoluble in all solvents. Like the phosphorus nitrides, it is very unreactive at moderately low temperatures. At a red heat, it is said to oxidize slowly in air to give phosphorus pentoxide. When heated with metals it forms phosphides, giving off ammonia in the process, thereby proving the presence of hydrogen in the structure. It reacts very slowly with boiling water, and the ammonium ion is said to be found in the resulting solution. From reading the literature it is difficult to tell whether or not the material described as phospham by one author is the same as the material described as a phosphorus nitride by another. Presumably, there are a number of highly polymerized amorphous compounds in the system P—N—H which have more or less hydrogen in their structure. According to Moureu and Rocquet,[145] the reaction product between ammonia and phosphorus pentachloride turns into phospham on heating in a vacuum. Further heating then gives the nitride for which the N/P mole ratio equals 1.7 which, on being heated still more, goes to the nitride with a N/P ratio near unity.

Materials with the formula PNO and PNS have been described occasionally.[60,117] These are generally obtained by heating the reaction product between ammonia and phosphoryl chloride or thiophosphoryl chloride under the proper conditions. The material with the empirical formula PNO is a very stable white powder with properties resembling those of phospham. PNS is also rather similar to phospham, although not quite so stable, since it appears that the sulfur can be substituted at least in part

[150] A. Stock and F. Wrede, *Ber.*, **40**, 2923 (1907); G. Wetroff, *Compt. rend.*, **213**, 780 (1941); S. Sato, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **34**, 888 (1938).

by oxygen under relatively mild conditions, such as boiling with water for a considerable length of time. Although complete x-ray data are not available, it would not be surprising to find that all the infusible white powders obtained by heating the reaction products of ammonia and various phosphorus halides or oxyhalides are amorphous, highly branched polymers in the system P—N—O—S—H in which there can be considerable variation of composition without much change in properties. A thorough reinvestigation from the polymer viewpoint of the various materials of this type reported in the literature is surely most desirable.

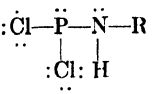
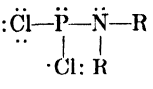
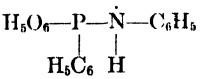
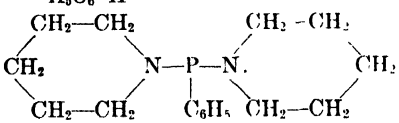
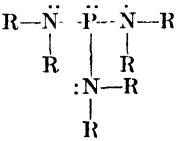
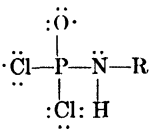
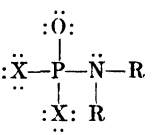
Organic Phosphorus-Nitrogen Compounds

Although the chemistry of organic compounds with phosphorus-to-nitrogen bonds has been studied since the latter part of the 19th century, there is still a great deal of confusion in the literature on the subject. Indeed, Kosolapoff has said: "Many of the rather interesting reactions used in the synthesis and interconversions in this family are very imperfectly understood. For this reason, a considerable degree of confusion exists in the literature on this subject to the present day. The elimination of such confusion is extremely necessary, and its accomplishment is one of the great challenges in the field of organophosphorus compounds."[83] He might also have added that the structures assigned to a number of organic compounds with P—N bonds are patently absurd.

The reader is referred to the works of Kosolapoff and of Fox and Lockhart[83] for a survey of the literature on this subject. However, the structures presented in these works and, indeed, all of the literature are not to be trusted since, in general, they result from organic chemical concepts of the late 19th century and reflect the confusion of that period with regard to the type of bonding exhibited by phosphorus in its compounds.

The various major classes of organic phosphorus-nitrogen compounds are listed in Tables 6-6 and 6-7. Table 6-6 is concerned with those compounds in which there is a single phosphorus atom, whereas Table 6-7 covers the compounds believed to be based on more than one phosphorus atom. Within both tables the substances are classified as to whether the phosphorus is connected to three or to four neighboring atoms. Usually, the decision as to whether the phosphorus is triply or quadruply connected was simple to make in the case of the compounds based on a single phosphorus atom, and the structures assigned in this book to these monophosphorus compounds are essentially the same as the structures assumed by the original investigators. However, the compounds listed in Table 6-7 as

TABLE 6-6
Organic Phosphorus-Nitrogen Compounds Based on a Single Phosphorus Atom

Item no.	Formula[a]	Examples	Descriptive name[b]	Typical reference
	Triply connected phosphorus			
1			Alkylaminophosphorus dichloride or alkylaminodichlorophosphine	151
2			Dialkylaminophosphorus dichloride or dialkylaminodichlorophosphine	151
3			Monophenylaminodiphenylphosphine	
4			Dipiperidylphenylphosphine	151
5			Trisdialkylaminophosphine or tri(dialkylamino)phosphine	151
	Quadruply connected phosphorus			
6		R = CH_3: liquid, b.p $_{7\ mm}$ = 132°C. R = C_5H_{11}: liquid, b.p $_{17\ mm}$ = 159°C.	Phosphoryl alkylamide dichloride	151
7		R = CH_3, X = Cl: liquid, b.p. = 195°C. R = C_2H_5, X = Br: undistillable oil R = C_6H_5, X = Cl: cryst., m.p. = 57°C.	Phosphoryl dialkylamide dichloride	151

(continued)

TABLE 6-6 (*continued*)

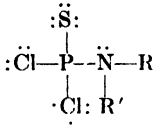
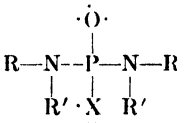
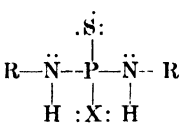
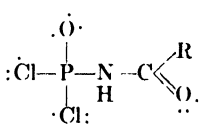
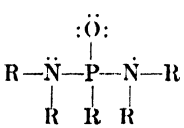
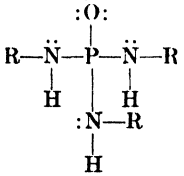
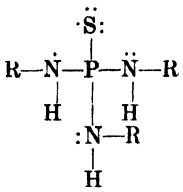
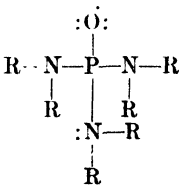
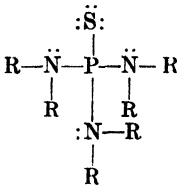
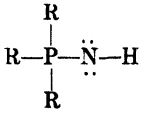
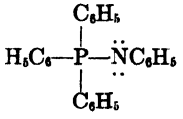
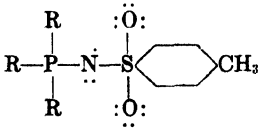
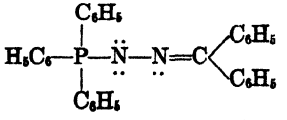
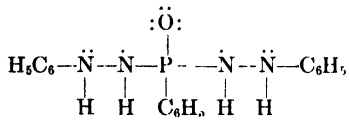
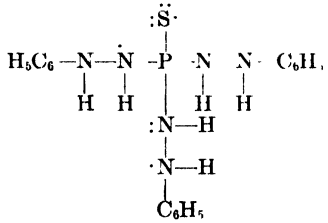
Item no.	Formula[a]	Examples	Descriptive name[b]	Typical reference
8		R = CH_3, R′ = H: liquid, b.p.$_{33\ mm}$ = 115°C. R = R′ = CH_3 liquid, b.p.$_{16\ mm}$ = 85–90°C.	Thiophosphoryl dialkylamide dichloride	151
9		R = C_2H_5, R′ = H, X = Cl. cryst. R = R′ = C_2H_5, X = F; cryst., liquid, b.p.$_{20\ mm}$ = 125°C	Phosphoryl bismonoalkylamide chloride	151
10			Thiophosphoryl bismonoalkylamide chloride	151
11		R = Cl_3C: cryst., m.p. = 146–148°C. R = C_6H_5: cryst., m.p. = 115°C., decomp. > ca 110°C	Phosphoryl acylamide dichloride	152
12			Alkylphosphoryl bisdialkylamide	151
13			Phosphoryl trismonoalkylamide	151

TABLE 6-6 (*continued*)

Item no.	Formula	Examples	Descriptive name	Typical reference
14			Thiophosphoryl trismonoalkylamide	151
15			Phosphoryl trisdialkylamide	151
16			Thiophosphoryl trisdialkylamide	151
17			Trialkylphosphinoimide	153
18			Triarylphosphinophenylimide	153
19			Trialkylphosphino-*p*-toluylsulfonimide	154
20			Triphenylphosphinodiazodiphenylmethane	155, 153

(*continued*)

TABLE 6-6 (*continued*)

Item no.	Formula[a]	Examples	Descriptive name[b]	Typical reference
21			Phenylphosphoryl bisphenylhydrazinide	156
22			Thiophosphoryl trisphenylhydrazinide	156

[a] Electron-pair bonds are shown by lines and unshared electrons by dots. All valence shell electrons are accounted for and every formula is written in accordance with the Octet Rule. π-Bonding is not shown here except between carbon and nitrogen or carbon and oxygen. Other π-bonds must be made by electron shifts.

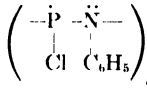
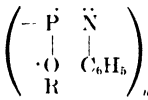
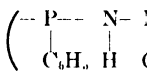
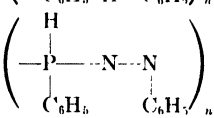
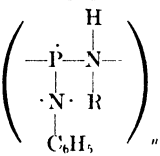
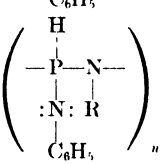
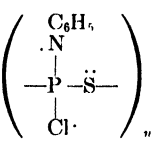
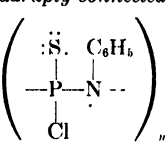
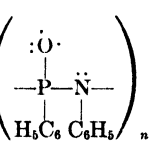
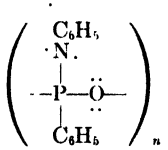
[b] These names are a personal preference, based on the long accepted nomenclature of inorganic phosphorus chemistry. For a discussion of the latest names recommended by official committees, see Anon., *J. Chem. Soc.*, **1952**, 5122; *Chem. Eng. News*, **30**, 4513 (1952); and L. Larsson, B. Holmstedt, and E. Tjus, *Acta Chem. Scand.*, **3**, 1563 (1954).

being based on more than one phosphorus atom have been quite uniformly described in the literature as structures based on one phosphorus atom having the right number of "multiple bonds" to fulfill the classical phosphorus "valence" of three or five, regardless of electronic structure. Although several of these compounds have been found to be dimers, the inference in the literature is that the dimerization may be a weak sort of affair, such as is found for, say, acetic acid in certain solvents.

Organic Phosphorus-Nitrogen Compounds Based on One Phosphorus Atom

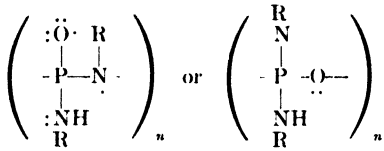
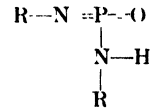
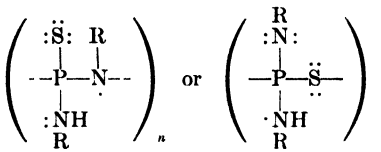
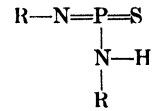
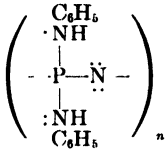
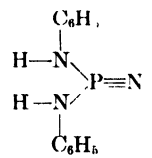
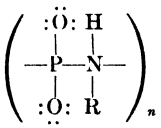
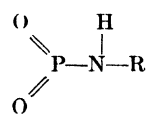
When the phosphorus trihalides are treated with primary or secondary amines, one halogen can be replaced by an amino group. The reactions are carried out in inert solvents, usually ether or ligroin, at room temperature or below, and the products are isolated after removal of the amine salt by filtration. Obviously, to obtain the amine salt, two moles of the amine

TABLE 6-7
Typical Organic Phosphorus-Nitrogen Compounds Presumed to be Based on More Than One Phosphorus Atom

Item no.	Monomeric segment[a]	Incorrect classical valence formula	Reference
	Triply connected phosphorus		
1		Cl—P=N—C_6H_5	144
2		RO—P=N—C_6H_5	144
	Triply or quadruply connected phosphorus		
3	 or 	H_5C_6—P=N—N—C_6H_5 (H)	143
4	 or 	H_5C_6—N=P—N(H)—R	145
	Quadruply connected phosphorus		
5	 or 	S—P(Cl)(—N—C_6H_5)—C_6H_5	159
6	 or 	O=P(—N—C_6H_5)—C_6H_5	159

(continued)

TABLE 6-7 (*continued*)

Item no.	Monomeric segment[a]	Incorrect classical valence formula	Reference
7			159
8			159
9			120 131
10			133

[a] See footnote *a* to Table 6-6 on page 336.

must be used per mole of phosphorus trihalide, as indicated by the following equation.

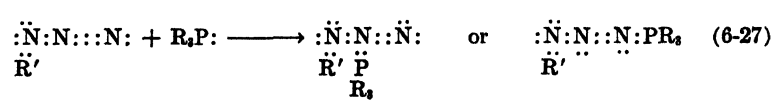
$$PX_3 + 2\,R_2NH \longrightarrow R_2NPX_2 + R_2NH{\cdot}HX \qquad (6\text{-}26)$$

Although the reactions with secondary amines proceed essentially as shown above, similar reactions with primary amines sometimes deviate considerably from the expected course. The initial reactions probably yield the expected products, but these compounds, in which the structure —N(H)—P(X)— appears, are very readily transformed into other substances by warming or by the presence of bases (for example, an excess of the amine). Usually the products of such a transformation are the compounds called "imidophosphites" by Kosolapoff, which are shown as item 4 in Table 6-7. Indeed, such transformations occur so readily in the case of primary aromatic amines that the initial reaction products have not been isolated. The known examples of this class of compounds are all mono-

alkylaminophosphorus dihalides. When phosphorus halides having more than one halogen atom (*i.e.*, PX_3 or RPX_2, but not R_2PX) are used in the reaction scheme which is idealized in equation 6-26, a mixture of products is usually obtained; however, the reaction can be controlled rather satisfactorily to give only a dialkylmonoamine of the phosphorus halide when disubstituted amines are employed. In this case, the amine hydrochloride is employed, and the mixture is refluxed for several hours.[151] The first two entries in Table 6-6 represent the reaction product of alkyl amines with phosphorus trichloride, of which a number of examples are known.[151] Examples 3 and 4 in Table 6-6 are also prepared by reacting the appropriate halide ($(C_6H_5)_2PCl$ in the case of item 3 and $C_6H_5PCl_2$ in the case of item 4) with the organic amine.

The organic phosphorus-nitrogen compounds in which the phosphorus atom is quadruply connected to the neighboring atoms are also often made by reacting the proper nitrogen base with a phosphorus halide, in this case the phosphoryl or thiophosphoryl halide. Thus, items 6, 7, 9, 11, 13, and 15 in Table 6-6 are made by direct reaction between the phosphoryl trihalide and the organic amine hydrochloride.[151] When the thiophosphoryl halide is used, one obtains Items 8, 10, 14, and 16. In reacting[152] phosphorus pentachloride with the amides of carboxylic acids one obtains substances of the general type $RC(Cl)=NP(O)Cl_2$. Exposure to moist air results in substitution of the Cl by OH to give acyl derivatives, as indicated by item 11 in Table 6-6.

The group of compounds shown as items 17–19 of Table 6-6 is usually known as the phosphinimines or phosphine imines. They are prepared by reacting tertiary phosphines with organic azides.[153] The first product formed by such a reaction is an adduct, two possible structures for which are indicated in equation 6-27.



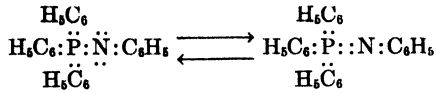
As a rule, these adducts must be prepared in the cold since, upon warming, they decompose with the loss of an N_2 molecule and the consequent formation of the respective phosphine imines. Presumably, the phosphine

[151] A. Michaelis, *Ann.*, **326**, 129 (1903); A. Michaelis and C. Roeber, *Ber.*, **31**, 1047 (1898).

[152] W. Steinkopf, *Ber.*, **41**, 3571 (1908).

[153] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921); H. Staudinger and J. Meyer, *ibid.*, **2**, 635 (1919).

imines exhibit an electronic structure approximated by the two assumed major resonating forms shown below:



(6-28)

A rather unusual phosphine imine is obtained by the reaction of chloroamine-T with tertiary phosphines.[154] When dry reagents are employed, true phosphine imines are formed. These compounds are based on the toluene sulfonamide radical, as indicated by item 19 in Table 6-6.

The phosphine imines, $R_3P(NR')$, react with a number of oxygen-containing compounds to give phosphine oxides. An example of this type of reaction is the hydrolysis shown in equation 6-29.

$$R_3P(NR') + H_2O \longrightarrow R_3PO + R'NH_2 \tag{6-29}$$

When R′ stands for an aliphatic group, the hydrolysis proceeds easily, so that the phosphine oxide results when such a phosphine imine is merely exposed to moist air. Hydrolysis does not take place nearly as readily in the case for which R′ is an aromatic group. In these instances the phosphine imines must be boiled in dilute acid in order that equation 6-29 be carried to completion. Several additional equations in which phosphine imines are reacted with oxygen-containing compounds are given below. Again, the aromatic compounds react less readily than the aliphatic.

$$\begin{aligned} R_3P(NR') + CO_2 &\longrightarrow R_3PO + R'NCO \\ R_3P(NR') + SO_2 &\longrightarrow R_3PO + R'NSO \\ R_3P(NR') + CS_2 &\longrightarrow R_3PS + R'NCS \end{aligned} \tag{6-30}$$

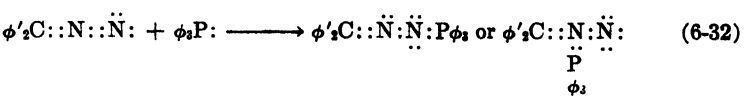
Typical organic reactions are

$$\begin{aligned} R_3P(NR') + C_6H_5NCO &\longrightarrow R_3PO + R'N{=}C{=}N(C_6H_5) \\ R_3P(NR') + (C_6H_5)_2C{=}C{=}O &\longrightarrow R_3PO + R'N{=}C{=}C(C_6H_5)_2 \end{aligned} \tag{6-31}$$

Item 20 in Table 6-6 is a phosphazine.[153,155] This type of compound is formed by combining an aromatic diazo compound with a triarylphosphine, as indicated in equation 6-32 below. It should be noted in this equation that two possible formulations are indicated for the phosphazine, the first one shown in the equation being the one assumed by Staudinger.[155]

[154] F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, **1937**, 527.

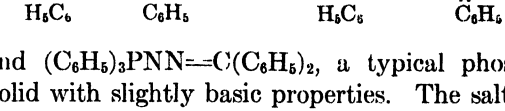
[155] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 612 (1919).



(6-32)

where ϕ stands for an aryl group.

Presumably, the structure of the phosphazines can be represented as a resonance hybrid of several electronic configurations, as shown below:



(6-33)

The compound $(C_6H_5)_3PNN{=}C(C_6H_5)_2$, a typical phosphazine, is a yellow, stable solid with slightly basic properties. The salts of this compound are colorless. They form by the mechanism of the hydrogen ion of an acid sharing a pair of previously unshared electrons on one or the other of the nitrogen atoms (see equation 6-33) so that the resulting $[(C_6H_5)_3PNHN{=}C(C_6H_5)_2]^+$ is a cation. The stability of the phosphazines is probably to be ascribed to the energy gained by the resonance shown in 6-33 plus resonance between a number of other possible forms not indicated there. Some of the phosphazines form derivatives other than the salts. Thus, a methyl iodide derivative is known. Presumably, in this derivative the electrons on the nitrogen are shared with the iodine atom.

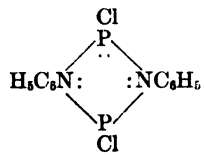
The halides of phosphorus can be reacted with organic derivatives of hydrazine, as well as with organic derivatives of ammonia. In this case, the compounds shown as items 21 and 22 in Table 6-6 are obtained.[156] The reaction between phenylhydrazine and, say, phosphoryl chloride is carried out in the cold in dry ether, with the usual six moles of base, phenylhydrazine, being used per mole of $POCl_3$ in order to tie-up the HCl resulting from the reaction. The product, $OP(NHNHC_6H_5)_3$, is soluble in alcohol and acetic acid but is not soluble in chloroform, ether, and benzene. It is quite stable in contact with water but decomposes at a moderate rate in acid or alkali.

Organic Phosphorus-Nitrogen Compounds Based on More Than One Phosphorus Atom

Prolonged heating of primary amines (or their hydrochlorides) with an excess of phosphorus trichloride results in a slow resolution of the amine hydrochlorides originally precipitated and subsequent formation of sub-

[156] A. Michaelis, *Ann.*, **293**, 193 (1896); *ibid.*, **294**, 1 (1896); A. Michaelis and F. Oster, *ibid.*, **270**, 126 (1892).

stances which the original authors have called phosphazo compounds. Thus, the compound with the empirical formula C_6H_5NPCl is formed by refluxing a mixture of aniline and phosphorus trichloride for several days, then boiling off the excess phosphorus trichloride and crystallizing.[157] Obviously, the classical valence formula shown for this compound—and, indeed, all of the classical valence formulas given in Table 6-7 for this general group of compounds—is incorrect. In the hypothetical monomeric C_6H_5NPCl, the phosphorus would be present as an sp or p^2-hybrid; but neither of these hybrids is found for phosphorus. Presumably, the compound should occur as the dimer of its empirical formula, and freezing-point measurements in benzene indicate that this is so.[157] This dimer should have the following structure:



(6-34)

Since triply connected phosphorus and triply connected nitrogen usually exhibit bond angles somewhat greater than 100° (so that the usual hybrid of these elements appears to be closer to sp^3 (with an abortive bond) than to p^3), it might be thought that a four-membered ring such as the one shown in equation 6-34 would exhibit considerable strain. However, the relatively high order of stability of the compound indicates that there is very little strain. Thus, we can tentatively conclude, on the basis of the dimeric formulation, that both phosphorus and nitrogen are present in this compound as rather pure p^3-hybrids with very little s-character. Treatment of $(C_6H_5NPCl)_2$ with sodium ethoxide gives the compound $[C_6H_5NP(OR)]_2$, which is listed in Table 6-7 as item 2. The parent compound, $(C_6H_5NPCl)_2$, is listed in this table as item 1.

As previously mentioned, $(C_6H_5NPCl)_2$ is a relatively stable substance. As might be expected, it is insoluble in water and does not react with cold water, even when quite finely divided. However on heating, the compound hydrolyzes according to the following over-all equation, in which intermediate products of hydrolysis are neglected.

$$(C_6H_5NPCl)_2 + 6\ H_2O \xrightarrow{\Delta} 2\ C_6H_5NH_2.HCl + 2\ H_2(O_3PH) \qquad (6\text{-}35)$$

An interesting reaction which is the reversal of the method whereby it is prepared has also been reported for $(C_6H_5NPCl)_2$. This reaction consists

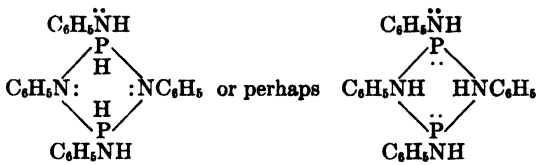
[157] A. Michaelis and G. Schroeter, *Ber.*, **27**, 490 (1894).

of dissolving the compound in benzene and treating it with dry hydrogen chloride according to the following over-all equation.

$$(C_6H_5NPCl)_2 + 6\ HCl \longrightarrow 2\ C_6H_5NH_2,HCl + 2\ PCl_3 \qquad (6\text{-}36)$$

By reacting phenyldichlorophosphine with phenylhydrazine, the compound shown as item 3 in Table 6-7 is obtained.[143] The exact placement of the hydrogen in this compound is difficult to establish. It could be on either one of the two nitrogen atoms in the monomeric segment shown in Table 6-7 or it could be on the phosphorus. If it is on the phosphorus, then this atom is quadruply connected, whereas if the hydrogen is on either of the nitrogen atoms the phosphorus is triply connected. Presumably, the hydrogen can move from one position to another, depending on the environment; and, indeed, there may well be an equilibrium between the forms corresponding to different placements of the hydrogen. It is to be expected that these compounds are dimers exhibiting the formula $(C_6H_5PNHNC_6H_5)_2$, which corresponds to a six-membered ring.

The compound with the empirical formula $C_6H_5NPNHC_6H_5$ has been studied quite recently, as compared to the other compounds in this class which were investigated around the turn of the century.[158] This compound, called phenylphosphazoanilide, as well as a similar compound, 2,2′-dimethoxyphenylphosphazoanilide having the empirical formula $[(CH_3O)C_6H_4]_2$-$PNHC_6H_5$, were both found to be dimers by freezing-point measurements in dioxane and bromoform, respectively. This means that the structural formula is the following:



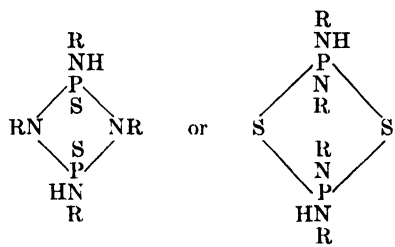
(6-37)

It is interesting to note that this compound can be made either directly from aniline and phosphorus chloride or by reacting $C_6H_5NPCl_2$ with aniline. This is proven by the fact that the two reaction products exhibited identical x-ray diffraction patterns.

When phosphoryl chloride or thiophosphoryl chloride is heated with a primary amine, compounds are formed in which the phosphorus atom is surrounded by four neighboring atoms. Typical of this class of com-

[158] W. H. Grimmel, A. Guenther, and J. F. Morgan, *J. Am. Chem. Soc* **68**. 539 (1946).

pounds[159] are items 5–8 of Table 6-7. Molecular weights have been measured on these compounds, and they, again, appear to be dimeric. In this case, it is much more difficult to conceive of a four-membered ring than in the case where the phosphorus was triply connected to its neighboring atoms. The detailed structure of one of these compounds should surely be studied by x-ray diffraction, in order to prove whether or not the ring is truly a four-membered one or—more likely—a six-membered one and whether either of the two alternative structures indicated in Table 6-7 and in equation 6-38 is the correct one. The dimer of the compound shown as item 8 in Table 6-7 is shown below:



(6-38)

The compounds described in Table 6-7 as items 9 and 10 are reaction products of the phosphonitrilic chlorides. These have been discussed in a previous section and appear to be based on six- and eight-membered rings as expected.

[159] A. Michaelis and W Karsten, *Ber.*, **28**, 1237 (1895); A. Michaelis, *Ann.*, **407**, 290 (1915).

CHAPTER 7

Lower Oxyacids of Phosphorus, Their Salts and Esters

HISTORY

Approximately a century after Boyle discovered phosphoric acid, le Sage[1] in 1777 made a mixture of oxyacids containing a large proportion of phosphorous acid. This acid, which was obtained by exposing sticks of elemental phosphorus to moist air and collecting the liquid formed, was at first confused with phosphoric acid. It was assumed that the difference between the acids was rather minor and depended solely on the rate of combustion of the phosphorus, so that phosphoric acid from rapid combustion was called *acidum phosphori per deflagrationem* and the mixture of lower oxyacids was called *acidum phosphori per deliquium*. It was not until 1812 that Davy[2] showed that a major constituent of the *acidum per deliquium* is a combination of phosphorous oxide and water (phosphorous acid) and is not simply a derivative of phosphoric oxide, such as is pyrophosphoric acid.

In the first half of the 19th century, a great deal of work was done on the completely inorganic oxyacids of phosphorus, and this work continued through the end of the century. However, study of the organic derivatives of the lower oxyacids of phosphorus did not achieve much momentum until the latter half of the 19th century. At the present time the emphasis is very much on the organic derivatives. During the century and a half that the lower oxyacids of phosphorus, their salts, and esters have been studied, a number of nonexistent compounds and false structures for existing compounds have been postulated. Indeed, even at the present time, there seems to be considerable misunderstanding as to which organic oxyacids of phosphorus and their derivatives are possible and which are not. However, an attempt will be made in this chapter to outline basic principles of structure by means of which absurd formulations can be ruled out and sensible predictions can be made.

[1] B. G. le Sage, *Mém. Acad.*, **1777**, 321

[2] H. Davy, *Phil. Trans*, **102**, 405 (1812).

The commonly known lower oxyacids of phosphorus exhibit structures in which only one phosphorus atom is involved. This is true only because most of the effort has been put on such compounds; and there is no question but that during the next century a larger number of lower oxyacids containing more than two phosphorus atoms per anion will be discovered, so that various homologous series of the lower oxyacids will become as well known as the series of chain and ring phosphoric acids are today. In some respects the little emphasis on lower oxyacids based on more than one phosphorus atom is surprising, since hypophosphoric acid, $(HO)_2(O)PP(O)(OH)_2$ —a lower oxyacid based on two phosphorus atoms—was discovered as early as 1877 by Salzer[3] in *acidum phosphori per deliquium*. However, it should be noted that only recently has it been conclusively demonstrated that this acid is a dimer of the simple empirical formula, H_2PO_3.

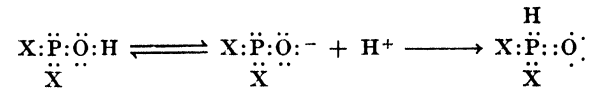
GENERAL DISCUSSION

The "lower oxyacids* of phosphorus" belong to the general class of oxyacids, in the anions of which a phosphorus atom is attached directly to a hydroxyl group which has a readily ionizable hydrogen atom that can be substituted by an organic radical to give an ester or by a cation to give a salt. In addition, there is at least one hydrogen, phosphorus atom, or organic group attached directly to at least one phosphorus atom in the anion of any lower oxyacid. In these acids and their derivatives, as in all other compounds of phosphorus, the most stable configuration of the phosphorus approximates sp^3-hybridization so that one would expect to find, in nearly every case, four neighboring atoms surrounding each phosphorus. As shown in Table 7-1, nearly all of the known phosphorus-based oxyacids, their salts, and esters in which there is a single phosphorus atom exhibit phosphorus which is quadruply connected. Indeed, when steps are taken to make an oxyacid based on triply connected phosphorus, it is found that the acidic hydrogen leaves its oxygen and becomes quite firmly affixed to the phosphorus through sharing of this atom's previously isolated pair of electrons. Thus, the completely substituted ester of phosphorous acid has the formula $P(OR)_3$, in which the phosphorus is triply connected,

[3] T. Salzer, *Liebig's Ann.*, **187**, 322 (1877); *ibid.*, **194**, 28 (1878); *ibid.*, **211**, 1 (1882); *ibid.*, **232**, 114 (1886).

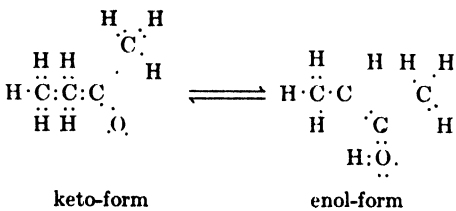
* It is unfortunate that the acid-base-salt nomenclature which originated in a primitive era of chemistry must be so overworked in this chapter. However, this nomenclature is so well ensconced that there is no alternative but to place emphasis on the term "acid"; although it is really the anion which is significant to this discussion, with little importance to be attached to the counter-ion—be it hydrogen or a metal ion.

although the free acid, the monoester, their salts, and the diester exhibit quadruply connected phosphorus, as indicated by the respective formulas: $H_2^{2+}(HPO_3)^{2-}$, $H^+[HPO_2(OR)]^-$, $HPO(OR)_2$. Organic chemists have likened this tautomeric rearrangement to a ketoenol shift, to which there is indeed a formal resemblance. An equation for the rearrangement is given below:



(7-1)

where X stands for any atom or radical attached to the phosphorus, and the π-character of the bonding in the product is formally depicted as being concentrated in P—O bond. The term "keto-enol shift" should not be used in referring to the hydrogen shift described in equation 7-1 because of the different kinds of π-bonding involved in the carbon and phosphorus compounds, as discussed in Chapter 3. Thus, the keto-enol shift in organic chemistry can be represented electronically as follows:



keto-form enol-form (7-2)

It should be noted that the second carbon atom from the left undergoes a radical change in the coördination number of its σ-bond base structure—going from a tetrahedral sp^3-hybrid to a triangular-planar sp^2-hybrid—in order to allow the π-bond (of unit intensity) to leave its original position between the third carbon and the oxygen atom and to re-form in a position between the second and third carbon atoms. In the case of the tautomeric rearrangement in the lower oxyacids of phosphorus, there is not much change in the σ-bond base structure of the phosphorus (with a hybrid lying between p^3 and sp^3 going to a more pure sp^3). Because of the reaction shown in equation 7-1, free acids based on triply connected phosphorus will be present only in extremely small amounts—amounts so small that they must be detected by very delicate methods (such as the interpretation of rate phenomena to show that such species play the role of activated complexes).

As might be expected, no oxyacids in which the phosphorus is connected to five or six neighboring atoms (approximating sp^3d- or sp^3d^2-hybridization of the phosphorus) have been discovered. However, it should be

TABLE 7-1
Oxyacids Based on One Phosphorus Atom, and Their Esters

No.	Empirical formulas: Condensed	Empirical formulas: Berselius	Correct chemical formula	Remarks	Nomenclature: Chemical Abstracts (until 1952)	Nomenclature: Kosolapoff (1951)	Nomenclature: British usage (until 1952)	Nomenclature: Beilstein, etc.	Nomenclature: 1952 Committee	Nomenclature: Van Wazer tradition-based name
1	R_2HPO	$4\ PR_3 \cdot 3\ H_2O \cdot P_2O_3$	H RPO R	Probably shows very weak acidity due to isomerization into $R_2PO^- + H^+$. Only a few, special examples known.	Dialkylphosphinous acid	Dialkylphosphinous acid, or secondary phosphinous acid	Dialkylphosphinous acid	Dialkylhydroxyphosphin	Dialkylphosphinous acid	Dialkylphosphine oxide
2	R_3PO	$4\ PR_3\ 3\ R_2O\ P_2O_3$	RPOR R	Triply connected phosphorous. About 20 examples known.	Alkyl dialkylphosphinite	Alkyl dialkylphosphinite	Alkyl dialkylphosphinite	Dialkylalkoxyphosphin	Alkyl dialkylphosphinite	Dialkylakoxyphosphine
3	H_3PO_2	$3\ H_2O \cdot P_2O$ or $PH_3 \cdot 3\ H_2O \cdot P_2O_3$	H HPO + H^+ O^-	Well known with proven structure. pK = 1 1	Hypophosphorous acid	Hypophosphorous acid	Hypophosphorous acid	Hypophosphorigsäure	Phosphinic acid (Used only for naming of organic derivatives, otherwise it is hypophosphorous acid)	Hypophosphorous acid
4	RH_2PO_2	$R_2O \cdot 2\ H_2O \cdot P_2O$ or $2\ PH_3 \cdot 3\ R_2O \cdot 3\ H_2O \cdot 2\ P_2O_3$	H HPOR O	Unknown, because of redox reactions in attempted preps.	Alkyl hypophosphite	Alkyl hypophosphite	Alkyl hypophosphite	Hypophosphorigsaure-alkylester, or alkylhypophosphit	Alkyl phosphinate	Alkyl hypophosphite
5	R_2HPO_2	$2\ R_2O \cdot H_2O \cdot P_2O$ or $PH_3 \cdot 3\ R_2O\ P_2O_3$	HPOR O R	Also an unknown ester.	Dialkyl hypophosphite	Dialkyl hypophosphite	Dialkyl hypophosphite	Hypophosphorigsäure dialkylester	Dialkyl phosphinate	Dialkyl hypophosphite, or more properly dialkoxyphosphine

6	RH_2PO_2	$R_2O \cdot 2\,H_2O\ P_2O$ or $2\,PH_2\ 3\,R_2O \cdot 3\,H_2O\ 2\,P_2O_3$	H RPO + H^+ O^-	About 30 examples known pK = ca. 1	Alkanephosphinic acid	Alkanephosphonous acid	Alkylphosphonous acid	Alkylphosphinigsaure	Alkylphosphinic acid	Alkylhypophosphorous acid
7	R_2HPO_2	$2\,R_2O\ H_2O\ P_2O$ or $PH_3\ 3\,R_2O\ P_2O_3$	H RPOR O	No well-established examples. Difficult to make	Alkyl alkanephosphinite	Alkyl alkanephosphonite	Alkyl alkylphosphonite	Alkylphosphinigsaure-alkylester	Alkyl alkylphosphinate	Alkyl alkylhypophosphite
8	R_3PO_2	$3\,R_2O\ P_2O$ or $PR_3 \cdot 3\,R_2O \cdot P_2O_3$	RPOR O R	Triply connected phosphorus About 5 examples known	Dialkyl alkanephosphonite	Dialkyl alkanephosphonite	Dialkyl alkylphosphonate	Alkylphosphinigsaure-dialkylester	Dialkyl alkylphosphonite	Dialkyl P-alkylhypophosphite or more properly alkyldialkoxyphosphine
9	R_2HPO_2	$2\,R_2O\ H_2O\ P_2O$ or $PH_3\ 3\,R_2O\ P_2O_3$	R RPO + H^+ O^-	Well known, a number of examples. pK = ca. 1	Dialkylphosphinic acid	Dialkylphosphonic acid or secondary phosphonic acid	Dialkylphosphonous acid	Dialkylphosphinigsaure	Dialkylphosphinic acid	Dialkylhypophosphorous acid
10	R_3PO_2	$3\,R_2O\ P_2O$ or $PR_3 \cdot 3\,R_2O\ P_2O_3$	R RPOR O	A number of examples known	Alkyl dialkylphosphinate	Alkyl dialkylphosphonate	Alkyl dialkylphosphonite	Dialkylphosphinigsäure-alkylester	Alkyl dialkylphosphinate	Alkyl dialkylhypophosphite
11	H_3PO_3	$3\,H_2O \cdot P_2O_3$	O HPO + $2H^+$ O^{2-}	$pK_1 = 1.3$, $pK_2 = 6.7$ A well-studied acid; structure recently well demonstrated	Orthophosphorous acid, or more usually phosphorous acid	Phosphorous acid	Phosphorous acid	Phosphorigsaure	Phosphonic acid (Used only for naming of organic derivatives, otherwise it is phosphorous acid.)	Orthophosphorous acid
12	RH_2PO_3	$RO_2\ 2\,H_2O\ P_2O_3$	R O HPO + H^+ O^-	pK = ca. 0.8 for ethyl derivative. Well known, many examples.	Alkyl phosphorous acid or monoalkyl phosphite	Alkyl phosphorous acid or monoalkyl phosphite	Alkyl phosphorous acid or monoalkyl phosphite	Phosphorigsäure-alkylester, or Alkylphosphit	Alkyl phosphonic acid	Alkyl orthophosphorous acid, or monoalkyl orthophosphite

(*continued*)

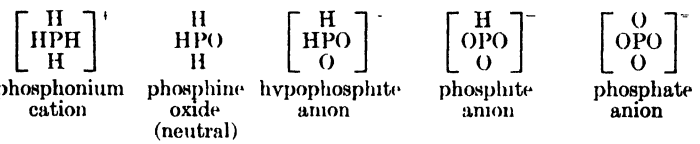
TABLE 7-1 (*continued*)

No.	Empirical formulas: Condensed	Empirical formulas: Berzelius	Correct chemical formula	Remarks	Nomenclature: Chemical Abstracts (until 1952)	Nomenclature: Kosolapoff (1951)	Nomenclature: British usage (until 1952)	Nomenclature: Beilstein, etc.	Nomenclature: 1952 Committee	Nomenclature: Van Wazer tradition based name
13	R_2HPO_3	2 $R_2O \cdot H_2O$ P_2O_3	R O HPOR O	Well known Very many examples	Dialkyl phosphite	Dialkyl phosphite	Dialkyl phosphite	Phosphorigsäure-dialkylester, or Dialkylphosphit	Dialkyl phosphonate	Dialkyl orthophosphite
14	R_3PO_3	3 R_2O P_2O_3	ROPOR O R	Triply connected phosphorus. Well established, with many examples known.	Trialkyl phosphite	Trialkyl phosphite	Trialkyl phosphite	Trialkylphosphit	Trialkyl phosphite	Trialkyl phosphite or more properly trialkoxyphosphine
15	RH_2PO_3	R_2O 2 H_2O P_2O_3	O RPO + 2 H^+ O^{2-}	Well known; many examples $pK_1 = 2.3$, $pK_2 = 8.0$ for ethyl derivative	Alkanephosphonic acid	Alkanephosphonic acid, or primary phosphonic acid	Alkylphosphonic acid	Alkylphosphonsäure	Alkylphosphonic acid	Alkylorthophosphorous acid
16	R_2HPO_3	2 R_2O H_2O P_2O_3	R O RPO + H^+ O^-	Well known, many examples. pK = ca 2 for diethyl derivative	Alkyl alkanephosphonic acid or monoalkyl alkane phosphonate	Alkyl alkanephosphonic acid or monoalkyl alkane phosphonate	Alkyl alkylphosphonic acid or monoalkyl alkylphosphonate	Alkylphosphonsaure-alkylester	Alkyl alkylphosphonic acid	Alkyl alkylphosphorous acid or monoalkyl alkylphosphite
17	R_3PO_3	3 R_2O P_2O_3	R O RPOR O	Many examples known	Dialkyl alkanephosphonate	Dialkyl alkanephosphonate	Dialkyl alkylphosphonate	Alkylphosphonsäure-dialkylester	Dialkyl alkylphosphonate	Dialkyl alkylorthophosphite

18	H_3PO_4 $3\,H_2O$ P_2O_5	O HOPO + 2 H^+ O^{2-}	Well known and established See Chapt 9 for details. pK_1 = 2.15, pK_2 = 7.2, pK_3 = 12.3.	Orthophosphoric acid—or, usually phosphoric acid	Phosphoric acid	Phosphoric acid	Phosphorsaure	Phosphoric acid	Orthophosphoric acid
19	RH_2PO_4 R_2O $2\,H_2O$ P_2O_5	O ROPO + 2 H^+ O^{2-}	Well known established. See Chapt. 9. pK_1 = 1.8. pK_2 = 7.0 for ethyl derivative	Alkylphosphoric acid or monoalkyl phosphate	Monoalkyl phosphate, primary ester of phosphoric acid	Monoalkyl phosphate, or alkyl phosphoric acid	Phosphorsaure-alkylester, or Alkylphosphat	Alkyl phosphoric acid	Alkyl orthophosphoric acid, or monoalkyl orthophosphate
20	R_2HPO_4 $2\,R_2O$ $H_2O \cdot P_2O_5$	R O ROPO + H^+ O^-	Well known and established See Chapt. 9. pK = 1.5 for diethyl derivative.	Dialkyl phosphoric acid or dialkyl phosphate	Dialkyl phosphate; secondary ester of phosphoric acid	Dialkylphosphate, or dialkyl phosphoric acid	Phosphorsaure-dialkylester, or Dialkylphosphat	Dialkyl phosphoric acid	Dialkyl orthophosphoric acid, or dialkyl orthophosphate
21	R_3PO_4 $3\,R_2O$ P_2O_5	R O ROPOR O	Well established. Very many examples known. See Chapt 9	Trialkyl phosphate	Trialkyl phosphate; tertiary ester of phosphoric acid	Trialkyl phosphate	Trialkylphosphat	Trialkylphosphate	Trialkyl orthophosphate

noted that a compound having the empirical formula of the ester of such a phosphoric acid, $P(OC_6H_5)_5$, has been reported.[4] It is thought that this compound is truly not an ester, in that the phosphorus is probably cationic instead of anionic, as indicated by the formula, $[P(OC_6H_5)_4]^+[C_6H_5O]^-$. This compound and similar ones are discussed in greater detail on p. 214.

For purposes of systematization, the generic structures of the oxyacid anions of phosphorus should probably be constructed from only phosphorus, oxygen, and hydrogen. By substituting oxygen and hydrogen around a quadruply connected phosphorus atom, we obtain the following series in which the third, fourth, and fifth members consist of anions. These three anions are the fundamental structures for all of the known oxyacids based on one phosphorus atom, as indicated in Table 7-1.



(7-3)

A number of organic derivatives can be derived by substituting alkyl or aryl groups for the hydrogen atoms directly attached to the phosphorus. These organic compounds, in the case of the hypophosphite and phosphite derivatives, bear conflicting names. Thus, the anion, $(R_2PO_2)^-$, is variously known as a dialkylphosphinate, dialkylphosphinite, dialkylphosphonate, and dialkylphosphonite. To further complicate the picture, it is shown that this acid can also very rightfully be considered as a *P,P*-dialkyl derivative of hypophosphorous acid. In the following text the nomenclature employed in industry and in the forthcoming second edition of the book by Kosolapoff[5] will be used, although the various organic acids will be discussed under the closest related inorganic acid of the series of three anions shown in series 7-3 above. In a concluding section of the first part of this chapter, the nomenclature of the organic acids of phosphorus will be discussed in considerably more detail.

Of the 21 types of compounds described in Table 7-1, ten are acidic, in that they exhibit considerable ionization of the hydrogen. These acidic compounds are items 3, 6, 9, 11, 12, 15, 16, 18, 19, and 20. Six of the ten

[4] L. Anschütz *et al.*, *Ann.*, **454**, 71 (1927).

[5] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, Chapt. VII, pp. 121-79, Chapt. VIII, pp. 180–210. (The nomenclature in the forthcoming second edition of this book will be basically unchanged. The major difference is that R_2PO_2H will be called "dialkylphosphinic acid" instead of "secondary phosphonic acid.") Also see a review by F. R. Atherton, *Quart. Rev.*, **3**, 146 (1949).

acidic compounds should be classified as acids, whereas the remaining four (numbers 12, 16, 19, and 20) are acid esters. Item 1 in Table 7-1 is also formally classed as an acid, following the terminology of most investigators in the field, although this compound, R_2HPO, is probably best characterized as a dialkylphosphine oxide. Fourteen esters (including the acid esters) are listed in Table 7-1. These esters are items 2, 4, 5, 7, 8, 10, 12, 13, 14, 16, 17, 19, 20, and 21. Again, items 2 and 5 are probably better characterized as dialkylalkoxyphosphine and dialkoxyphosphine, respectively, than as the esters of an acid

ACIDS, SALTS, AND ESTERS BASED ON ONE PHOSPHORUS ATOM

"Phosphinites," $R_2P(OR)$

The tautomeric forms of dialkylphosphine oxide or diarylphosphine oxide would have an —OH group attached to a triply connected phosphorus atom and hence should formally exhibit the structure of an acid, which is generally called phosphinous acid, R_2POH. The "esters" of this "acid" are derivatives of phosphine and thus also can be called dialkylalkoxyphosphines (where any or all of the alkyl radicals can be substituted by aryl radicals). Nearly 20 of these "esters," $R_2P(OR)$, have been described[5–7] in the literature. Two techniques have generally been used in their preparation. They consist of the reaction of organic monohalophosphines with phenols[8] and with sodium alkoxides.[9] In the case of the attempted preparation of a number of these compounds—especially the methyl and benzyl "esters"—immediate isomerization[9] to the corresponding phosphine oxides takes place, $R_2P(OR) \rightarrow R_3PO$.

The "phosphinite esters," which have the empirical formula, R_3PO, are isomeric with the phosphine oxides, which have been discussed on pp. 286–289. These two classes of isomers do represent decidedly different compounds, since most of the "phosphinite esters" are liquids at room temperature, whereas phosphine oxides of the same empirical composition are solids. This is shown in Table 7-2. The "phosphinite esters" readily undergo isomerism either internally[10] or by reaction[9] with alkyl halides to

[6] V. N. Plets, Ph.D. Thesis, Univ. of Kazan, Kazan, Russia, 1938.

[7] R. B. Fox and L. B. Lockhart, *The Chemistry of Organo-Phosphorus Compounds*, Naval Research Laboratory, Washington, D. C., July 8, 1948 (NRL Rept. C-3323).

[8] A. Michaelis, *Ann.*, **315**, 43 (1901).

[9] A. E. Arbusov, *J. Russ. Phys.-Chem. Soc.*, **42**, 395 (1910); A. E. Arbusov and A. I. Razumov, *J. Gen. Chem (U.S.S.R.)*, **4**, 834 (1934); A. E Arbusov and N. Nikonorov, *Zhur Obscheĭ Khim.*, **18**, 2008 (1948).

[10] A Michaelis and L Gleichmann, *Ber*, **15**, 801 (1882).

TABLE 7-2
Comparison of R_2PO Isomers

"Phosphinite esters"	Phosphine oxides
$CH_3(C_2H_5)P(OC_2H_5)$	$CH_3(C_2H_5)_2PO$
Liquid, b.p.$_{15\ mm}$ = 67–70°C.	Solid, sublimes
$(C_2H_5)_2P(OC_2H_5)$	$(C_2H_5)_3PO$
Liquid, b.p.$_{15\ mm}$ = 80–5°C.	Crystals, m.p. = 48 ± 2°C., b.p. = 240 ± 3°C.
$(C_6H_5)_2P(OC_6H_5)$	$(C_6H_5)_3PO$
Liquid, b.p.$_{62\ mm}$ = 265–70°C., d_4^{21} = 1.140	Solid, m p. = 153°C., b.p. = 360°C.
$C_2H_5(C_6H_5)P(OC_2H_5)$	$(C_2H_5)_2(C_6H_5)PO$
Liquid, b.p.$_{15\ mm}$ = 137–42°C	Crystals, m.p. = 55–7°C , b p > 360°C
$(C_6H_5)_2P(OCH_3)$	$(C_6H_5)_2(CH_3)PO$
Liquid, b.p.$_{10\ mm}$ = 151–2°C., d_0^{15} = 1 104 n_D^{20} = 1 6030	Crvstals, m.p. = 110 ± 2°C
$(C_6H_5)_2P(OC_2H_5)$	$C_2H_5(C_6H_5)_2PO$
Liquid, b.p.$_{15\ mm}$ = 137–42°C.	Crystals, m.p. = 121°C.

yield the phosphine oxides. The reaction with alkyl halides is depicted below as proceeding via an intermediate phosphonium compound, which has been isolated[11] in two cases: $[(C_6H_5)_2(C_6H_5CH_2)P(OC_6H_5)]^+Cl^-$ and $[(C_6H_5)_2CH_3P(OC_6H_5)]^+I^-$. These two isolated intermediates are found to react with water or alkaline solutions to give the same phosphine oxides as produced in the isomerization equation below.

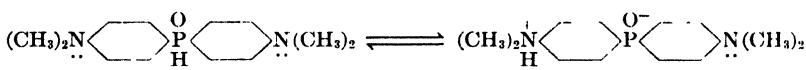
$$R_2POR' + R''X \longrightarrow (R_2R''POR')^+X^- \rightleftharpoons \underset{\text{activated complex}}{[R_2R''PX(OR')]} \longrightarrow R_2R''PO + R'X \quad (7\text{-}4)$$

An indication that the so-called "phosphinite esters" are truly phosphine derivatives is evidenced by their reaction with sulfur or selenium to give[11] the corresponding phosphine sulfides or selenides, $R_2(RO)PS$ and $R_2(RO)$-PSe. The "phosphinite" esters also form addition products[9] with cuprous halides, as is generally the case with compounds exhibiting triply connected phosphorus and hence an unshared pair of electrons.

Saponification[11] of the "phosphinite esters," as well as hydrolysis[8,10] of the monohalophosphines does not give the free "phosphinous acid," but instead leads to a mixture of the corresponding secondary phosphine, R_2PH, and the phosphinic acid, $R_2PO(OH)$. However, two "phosphinous acids" have been isolated in the free state. In both of these acids, one of the organic radicals attached directly to the phosphorus is a complicated

[11] A. Michaelis and W. La Coste, *Ber.*, **18**, 2109 (1885).

nitrogen-containing aryl group. These two isolated compounds are bis(*p*-dimethylaminophenyl)phosphinous acid[12] (crystallized from benzene, m.p. 169°C.) and 5,10-dihydro-10-phenolphosphazinous acid[13] (needles from dilute ethyl alcohol, decomp. at 215°C.). The first of these compounds, $[4\text{-}(CH_3)_2NC_6H_4]_2POH$, has been made by hydrolysis of the reaction mixture obtained from phosphorus trichloride and dimethylaniline. It appears that the tertiary amine in the structure somehow stabilizes this "free phosphinous acid," perhaps by forming a quaternary cation and thereby completely removing the hydrogen from the vicinity of the phosphorus atom, so that it can no longer play a role in the tautomeric shift between the oxygen attached directly to the phosphorus and the otherwise unshared pair of electrons on the phosphorus, viz.:



(7-5)

It is interesting to note that this free phosphinous acid is readily oxidized[12] by oxygen or air to the corresponding phosphinic acid, $[4\text{-}(CH_3)_2NC_6H_4]_2PO(OH)$.

Preparation and Structure of Hypophosphorous Acid and Its Salts

Of the three fundamental acids based on one phosphorus atom (hypophosphorous, phosphorous, and phosphoric acids), the hypophosphorous acid is the more difficult to prepare in good yield. Commercial manufacture[14] of the hypophosphites is usually carried out by treating white phosphorus with a boiling slurry of lime. (In the laboratory, barium hydroxide is often employed instead of lime.[15]) In addition to calcium hypophosphite, which remains in solution, insoluble calcium phosphite is formed, along with phosphine (containing sufficient diphosphine to make it spontaneously flammable) and hydrogen. The mechanism of this complicated reaction

[12] M. Bourneuf, *Bull. soc chim. France*, **33**, 1808 (1923); H. Raudnitz, *Ber.*, **60**, 743 (1927).

[13] P. G. Sergeev and D. G. Kudryashov, *Zhur. Obshchet Khim.*, **8**, 266 (1938); A. Michaelis and A. Schenk, *Ber.*, **21**, 1497 (1888).

[14] J. R. Van Wazer, *Encyclopedia of Chemical Technology*, ed., R. E. Kirk and D. F. Othmer, Interscience Publishers, New York, 1953, Vol. 10, pp. 488–94; G. M. Kosolapoff, ibid., Vol. 10, pp. 494–505; B. Topley and B. Raistrick, *Thorpe's Dictionary of Applied Chemistry*, ed., M. A. Whiteley, A. J. E. Welch, and L. N. Owen, Longmans Green & Co., London, Vol. 9, pp. 502–08.

[15] D. M. Yost and H. Russell, *Systematic Inorganic Chemistry*, Prentice-Hall Inc., New York, 1946, Chapt. 6, pp. 191–209.

is imperfectly understood at present. Under some conditions, equal amounts of phosphorus appear as phosphine and as phosphite, and the volume of hydrogen liberated is nearly proportional to the hypophosphite formed. These generalizations apply to both calcium and sodium hydroxides as a source of the hydroxyl ion and agree approximately with the following equations.

$$P_4 + 4\,OH^- + 4\,H_2O \longrightarrow 4\,H_2PO_2^- + 2\,H_2\uparrow \qquad (7\text{-}6)$$

$$P_4 + 4\,OH^- + 2\,H_2O \longrightarrow 2\,HPO_3^{2-} + 2\,PH_3\uparrow \qquad (7\text{-}7)$$

In addition, there also appears to be a small amount of decomposition[16] of the hypophosphite anion by the alkali

$$H_2PO_2^- + OH^- \longrightarrow HPO_3^{2-} + H_2\uparrow \qquad (7\text{-}8)$$

In this method of preparation any excess calcium hydroxide is precipitated by carbon dioxide, and the calcium carbonate is removed by filtering. The filtered solution is then carefully evaporated under reduced pressure (temperature $< 45°C.$) to give crystals of calcium hypophosphite. If these crystals are dissolved in water and the solution is treated with an equivalent amount of sulfuric acid or sodium sulfate, the free acid or sodium salt, respectively, is produced.

An interesting laboratory procedure for the preparation of hypophosphorous acid consists of oxidizing phosphine in an aqueous suspension of iodine.[17] The phosphine, made from calcium phosphide and dilute hydrochloric acid, is passed into a flask containing the agitated iodine suspension until the color of the iodine is discharged. Repeated distillation under reduced pressure (40 mm. Hg) removes the HI and H_2O, leaving pure hypophosphorous acid, $H(O_2PH_2)$, as the residue. Hypophosphorous acid is also formed when white phosphorus is slowly oxidized in the presence of water. However, the yield is relatively small so that, when white phosphorus is oxidized by passing moist air over it, only 10–12% of the original phosphorus occurs as hypophosphorous acid.[18] Hypophosphorous acid is also produced when certain phosphides, such as those of the alkaline earth metals, are decomposed by water. A technique for purifying crude hypophosphorous acid has recently been described.[19] Purification is achieved by repeated filtration of crystals from the concentrated acid.

[16] The kinetics of this reaction has been studied by A. Sieverts and F. Loessner, *Z. anorg. Chem.*, **76**, 10 (1912).

[17] R. Paris and P Tardy, *Compt. rend*, **223**, 242 (1946).

[18] T. Milobedzki and M. Makulec, *Roczniki Chem.*, **23**, 13 (1949).

[19] W. A. Jenkins and R T. Jones, *J Am. Chem. Soc.*, **74**, 1353 (1952).

A number of salts of hypophosphorous acid have been prepared,[20] some of them quite recently.[21] In general, the hypophosphite salts are made by merely mixing the metal oxide or hydroxide with hypophosphorous acid. In many cases, when the metal can readily be reduced, a redox reaction occurs instead of salt formation. Examples are found in the case of copper and silver. However, it is sometimes possible to make such salts by keeping the solutions refrigerated and/or rapidly precipitating the solid salt by addition of alcohol.[22] No esters of hypophosphorous acid have as yet been characterized. The problem here appears again to be one of unwanted oxidation of the hypophosphite.[23]

The structure of the hypophosphite anion has been shown by an x-ray diffraction study of ammonium hypophosphite to consist of a distorted tetrahedron in which two corners are occupied by oxygen atoms and the other two by hydrogen atoms, with the phosphorus atom being in the center of the tetrahedron.[24] In this work the P-O distance was found to be 1.51 A. and the P-H distance about 1.5 A., with the O—P—O angle being 120° and the H—P—H angle being 92°. Magnesium, nickel, and cobalt hypophosphite hexahydrate have also been investigated by x-rays.[25] This work shows that in the magnesium salt the $H_2PO_2^-$ anion is roughly tetrahedral, with P-O distances of 1.52 A. and an O—P—O angle of 109°. The measured P-O distances correspond to approximately 0.6 π-bond per σ-bond —a value which is equivalent to 1.2 π-bonds per phosphorus atom.

The nuclear magnetic resonance spectrum[26] of phosphorus in solutions of the hypophosphites exhibits 1-2-1 spin-spin splitting with a separation

[20] For a review of the early literature, see J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1928, Vol VIII, pp. 870–99 (hypophosphorous acid and the hypophosphites), pp 899–922 (phosphorous acid and the phosphites), pp 924–40 (hypophosphoric acid and the hypophosphates).

[21] D. A. Everest, *J. Chem. Soc.*, **1952**, 2945 (aluminum); E. Einecke, *Die Chemie*, **55**, 40 (1942) (gallium), F. Ensslin, H. Dreyer, and O. Lessmann, *Z. anorg. Chem.*, **254**, 315 (1947) (indium); W. A. Jenkins and D. M. Yost, *J. Am. Chem. Soc.*, **73**, 2945 (1951); A. Ferrari and C. Colla, *Gazz. chim. ital.*, **67**, 88 (1937) (thallium); D. A. Everest, *J. Chem. Soc.*, **1952**, 1670 (germanium); *ibid.*, **1951**, 2903; *ibid.*, **1954**, 4698 (tin); R. Castagnou and G. Ducleon, *Bull. trav. soc. pharm. Bordeaux*, **88**, 18 (1950) (titanium).

[22] For example, see R. Engel, *Compt. rend.*, **129**, 518 (1899) ($Cu(H_2PO_2)_2$).

[23] R. Fosse, *Bull. soc. chim. France*, **7**, 228, 231, 357 (1910) (action of alcohols, aldehydes, and ketones). J. Mai, *Ber.*, **35**, 162 (1902) (hypophosphorous acid converts diazo compounds into hydrocarbons).

[24] W. H. Zachariasen and R. C. L. Mooney, *J. Chem. Phys.*, **2**, 34 (1934); M. L. Huggins, *Phys. Rev.*, **21**, 719 (1923).

[25] A. Rodríguez Pedrazuela, S. Garcia-Blanco, and L. Rivoir, *Anales real soc. españ. fis. y quím. (Madrid)*, **49A**, 255 (1953). A. Ferrari and C. Colla, *Gazz. chim. ital.*, **67**, 294 (1937).

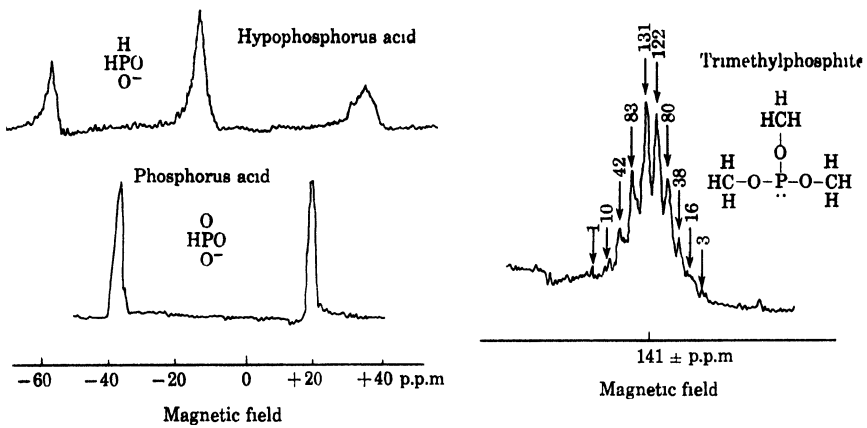


Fig 7-1 The phosphorus nuclear magnetic resonance spectra of the hypophosphite and phosphite anions and trimethyl phosphite The hypophosphite anion exhibits a spectrum with three peaks of relative intensities 1-2-1, the phosphite anion two equal peaks, and trimethyl phosphite nine peaks of theoretical relative intensities 1-9-36-84-126-84-36-9-1. The multiplet structure of the spectra is due in all cases to indirect spin-spin splitting by the covalently bonded hydrogen atoms

between individual resonance peaks of 0.33 gauss, as is shown in Figure 7-1 Likewise, the hydrogen spectrum has two peaks, corresponding to 1-1 spin-spin splitting. This means that the two hydrogen atoms (nuclear spin = $^1/_2$) are covalently bonded to the phosphorus atom (nuclear spin = $^1/_2$), and that, if there is any exchange of these hydrogens with each other or with the water, the rate of exchange is reasonably slow (half life $\geq$ mins.). According to these measurements, approximately 95% or more of the free acid or its salts is present in the form in which four atoms are attached directly to the phosphorus. Raman spectral measurements have been carried out on hypophosphorous acid and some of its salts.[27,28] These

[26] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. S. Gutowsky and D. W. McCall, *ibid*, **22**, 162 (1954); J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956); W. E. Quinn and R. M. Brown, *J. Chem. Phys.*, **21**, 1605 (1953).

[27] M. Tsuboi, *J. Am. Chem. Soc.*, **79**, 1351 (1957); T. J. Hanwick and P. O. Hoffmann, *J. Chem. Phys.*, **19**, 708 (1951); J. P. Mathieu and J. Jacques, *Compt. rend.*, **215**, 346 (1942); A. Simon and F. Feher, *Z. anorg. u. allgem. Chem.*, **230**, 289 (1937); J. C. Ghosh and S. K. Das, *J. Phys. Chem.*, **36**, 586 (1932).

[28] For infrared data, see D. E. C. Corbridge and E. J. Lowe, *J. Chem Soc.*, **1954**, 493; L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951); *Infrared Spectra of Phosphorus Compounds;* Naval Research Laboratories, Washington, D C., 1950 (NRL Rept. No. 3657).

studies show that the hypophosphite ion exhibits C_{2v} symmetry, which is the symmetry to be expected for a tetrahedral $H_2PO_2^-$ anion.

In spite of the fact that the acid, its alkali metal, and alkaline earth metal salts are found—within the precision of the various measurements—to exist wholly in the form based on quadruply connected phosphorus, it is possible the equilibrium between the tautomeric forms can be strongly shifted toward the form based on triply connected phosphorus. This might occur under conditions in which an electron acceptor other than the hydrogen ion can share the otherwise unused pair of electrons on the triply connected phosphorus atom. Perhaps such conditions are met in the adducts or double salts of stannous hypophosphite with stannous bromide or iodide.[29]

Physical Properties and Reactions of Hypophosphorous Acid and Its Salts

Pure hypophosphorous acid, $H(O_2PH_2)$, is a white crystalline solid which melts at 26.5°C. In order to avoid rapid decomposition it should not be heated above 100°C., or preferably above 50°C. The heat of fusion of the acid is 2.4 kcals./mole, and the heat of solution of the crystalline acid in water is about −0.18 kcal./mole.[30] The acid is easily supercooled and can be obtained as a very viscous liquid, or as a glass at sufficiently low temperatures. Hypophosphorous acid is a strong monobasic acid in which only one hydrogen can be substituted by a metal ion. Its dissociation constant has been measured[31] and found to be 8.0×10^{-2}, as recalculated from the data given by Kolthoff. The fact that hypophosphorous acid is monobasic lends support to the structure based on quadruply connected phosphorus. A titration curve of hypophosphorous acid is presented in Figure 7-2, along with curves for some other lower oxyacids of phosphorus. The dissociation constant of hypophosphorous acid has been compared with the dissociation constants of other oxyacids and its value has also been derived from theoretical equations for such constants.[32] In Table 7-3 the thermodynamically correct dissociation constants of a number of the oxyacids of phosphorus are compared with each other.

[29] D. A. Everest, *J. Chem. Soc.*, **1954**, 4698.

[30] J. Thomsen, *Ber.*, **7**, 994, 996 (1874); *J. prakt. Chem.*, **11**, 133 (1875); *Thermochem. Untersuch.*, **1**, 178, 195, 297 (1883); *ibid.*, **2**, 212, 225 (1884).

[31] I. M. Kolthoff, *Rec. trav. chim.*, **46**, 350 (1927); W. V. Bhagwat and N. R. Dhar, *J. Indian Chem. Soc.*, **6**, 781 (1929); C. Morton, *Pharm. J.*, **125**, 102 (1930); *Chemist and Druggist*, **113**, 138 (1930); A. D. Mitchell, *J. Chem. Soc.*, **117**, 957 (1920). For recalculation of Kolthoff's data, see ref. 34.

[32] J. E. Ricci, *J. Am. Chem. Soc*, **70**, 109 (1948); G. Schwarzenbach. *Helv. Chim. Acta*, **19**, 1043 (1936).

The known[20] alkali metal hypophosphites and related salts are $Li(O_2PH_2)\cdot H_2O$, $Na(O_2PH_2)\cdot H_2O$, $K(O_2PH_2)$, $NH_4(O_2PH_2)$, and $(NH_3OH)(O_2PH_2)$. They are all very soluble in water. However, solubility data have not been reported[33] for them except in the case of the sodium salt in

TABLE 7-3
Ionization Constants[a] of Various Oxyacids of Phosphorus at 20–25°C.[34]

Acid	Formula	pK_1	pK_2	pK_3	pK_4
Hypophosphorous	$H^+ + H_2PO_2^-$	1 1			
Phosphorous	$2\,H^+ + HPO_3^{2-}$	1 3	6 7		
Monoethyl phosphite	$H^+ + (RO)HPO_2$	0 8			
Methanephosphonic	$2\,H^+ + RPO_3^{2-}$	2 3	7 9		
Propanephosphonic	$2\,H^+ + RPO_3^{2}$	2 4	8 2		
Phosphoric	$3\,H^+ + PO_4^{3-}$	2 1	7 1	12 3	
Monoethyl phosphate	$2\,H^+ + (RO)PO_3^{2-}$	(1 8)	7 0		
Diethyl phosphate	$H^+ + (RO)_2PO_2^-$	(1 5)			
Hypophosphoric	$4\,H^+ + {}^{2-}O_3PPO_3^{2-}$	(2 0)?	(2 6)?	7 2	10 0
Pyrophosphoric	$4\,H^+ + {}^{2-}O_3POPO_3^{2-}$	1 0	2 0	6 6	9 6

[a] The constants listed here are the best values for the thermodynamic ionization constants Values given in parentheses were crudely estimated from apparent dissociation constants uncorrected for activities The values for hypophosphoric acid, which result from pH measurements, are believed to be too high, according to available freezing-point data

two glycols.[35] The alkaline earth metal phosphates[20] are $Mg(O_2PH_2)_2\cdot 6H_2O$, $Ca(O_2PH_2)_2$, $Sr(O_2PH_2)_2$, $Ba(O_2PH_2)_2$, and $Ba(O_2PH_2)_2\cdot H_2O$. These salts are also quite soluble in water, the solubility of $Ca(O_2PH_2)_2$ and $Ba(O_2PH_2)_2\cdot H_2O$ being[20] about 17 g. and 29 g., respectively, per 100 g. H_2O at room temperature. As one would expect, the hydroxylamine salt detonates[20] when heated to about 100°C.

The hypophosphites and phosphites form solid addition products[36] with the hydrogen halides, HCl, HBr, and HI. Although phosphates can add three moles of the hydrogen halide, the hypophosphites and phosphites are like the sulfates in that they add two moles of the hydrogen halide. A

[33] Heats of solution are given for the Na, NH_4, Ca, and Ba salts by N. F. H. Bright and T. Carson, *Can. J. Technol.*, **31**, 221 (1953).

[34] T. D. Farr, *Phosphorus, Properties of the Element and Some of Its Compounds*, Tenn Valley Authority, Wilson Dam, Ala., 1950 (*TVA Chem. Eng. Rept. No. 8*).

[35] At 25°C., $Na(O_2PH_2)$ is soluble to the extent of 33.01 g./100 g. of ethylene glycol and 9.70 g./100 g. of propylene glycol, according to S. R. Palit, *J. Am Chem. Soc.*, **69**, 3120 (1947).

[36] F. Ephraim and A. Scharer, *Ber.*, **61B**, 2161 (1928).

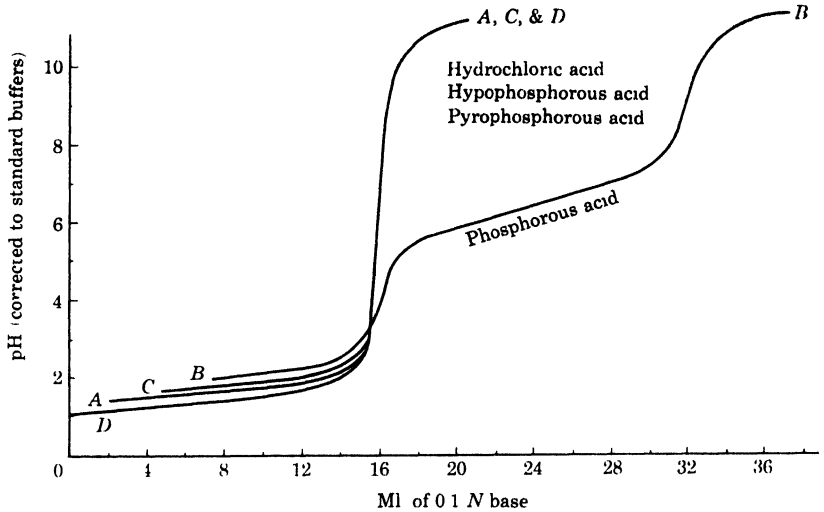


Fig. 7-2. pH titration curves of: (*A*) hypophosphorous acid, (*B*) phosphorous acid, (*C*) pyrophosphorous acid, and (*D*) hydrochloric acid.

typical hypophosphite addition product of this type is $Cd(H_2PO_2)_2 \cdot 2\,HCl$. In these compounds the hydrogen halide is presumably held in the same manner as hydrogen oxide in the hydrates, *i.e.*, coordinated to the metal ion

The kinetics of isotope exchange of the hypophosphites with water and the hypophosphites with the salts of other oxyacids of phosphorus has been rather thoroughly investigated. The early studies[37] indicated that the two hydrogens directly attached to the phosphorus on the hypophosphite anion did not exchange with the hydrogen of water. However, recent investigations[38] show that this exchange, although slow, is measurable. The rate, R, at which there is exchange of one such hydrogen (bonded directly to the phosphorus) per hypophosphite anion is given by the following equation, in which the numerical constants refer to a temperature of 30.0°C.

$$R = 3.33(H^+)(H_2PO_2)^- + 2.9(H_3PO_2)^2 \qquad (7\text{-}9)$$

[37] H. Erlenmeyer, W. Schoenauer, and G. Schwarzenbach, *Helv. Chim. Acta*, **20**, 726 (1937); H. Erlenmeyer and H. Gärtner, *Nature*, **134**, 327 (1934).

[38] W. A. Jenkins, Jr., and D. M. Yost, *J. Chem. Phys.*, **20**, 538 (1952); A. I. Brodskiĭ and L. V. Sulima, *Doklady Akad. Nauk S.S.S.R.*, **85**, 1277 (1952).

where R is measured in l./mole/hr. This exchange is believed to be dependent on a slow process whereby the usual tautomeric form of the anion transforms to the form based on triply connected phosphorus. Exchange of oxygen between the hypophosphite ion and the water in which it was dissolved has also been investigated.[39] The half-life for oxygen exchange was shown to be 70 hr. and <0.2 hr. in the case of the acid at 40° and 100°C., respectively. The rate of oxygen exchange was so slow for the sodium salt that it could not be detected even at 100°C. These values should be compared with the half-lives for exchange of the bonded hydrogens, as measured[38] by the same authors, viz. 16 min. for $H(O_2PH_2)$ at 25°C. and 21 hr. for $Na(O_2PH_2)$ at 100°C. Presumably, the slower rate of oxygen exchange for the sodium salt as compared to the acid is due to hydrogen bonding between the —OH groups of the acid and the water. This assumes a mechanism for the exchange process somewhat like the Grotthuss chain theory of electrical conductivity.[40] On the basis of this hypothesis, it appears that the hydrogens attached directly to the phosphorus atom form much weaker hydrogen bonds with water than do the —OH hydrogens.

Phosphorus is found[41] to exchange neither between hypophosphites and phosphites nor between hypophosphites and phosphates, in acid or neutral solution. It is interesting to note that exchange between hypophosphorous acid and phosphorous acid is also absent in the presence of iodine or iodides, although the reaction whereby hypophosphorous acid is oxidized to phosphorous acid with concomitant reduction of iodine ought to result in a rate of phosphorus exchange which would be comparable to the rate of the redox reaction. In the case of mixtures of arsenous and arsenic acids, iodine does promote exchange of arsenic at the rate predicted from the kinetics of the redox reaction. The lack of exchange between hypophosphorous acid and phosphorous acid in the presence of iodine is explained by assuming that there is a slow rate of transformation from an inactive into an active form of hypophosphorous acid, followed by a fast, irreversible oxidation of the active form of the acid by iodine. In such a case, the first reversible process cannot give rise to exchange and the second (redox) process would not be accompanied by an exchange of phosphorus because of its irreversibility. Presumably, the active form of hypophosphorous acid is the tautomer based on triply connected phosphorus. This result and the finding with respect

[39] A. I. Brodskii and L. V. Sulima, *Doklady Akad. Nauk S.S.S.R.*, **92**, 589 (1953).

[40] S. Glasstone, *Textbook of Physical Chemistry*, 2nd ed., D. Van Nostrand Co., Inc., New York, 1946, pp. 887, 898.

[41] A. I. Brodskiĭ, D. N. Strazhesko, and L. L. Chervyatsova, *Doklady Akad. Nauk S.S.S.R.*, **75**, 823 (1950); V. D. Ionin, A. F. Lukovnikov, M. B. Neiman, and An. N. Nesmeyanov, *ibid.*, **67**, 463 (1949); C. Perrier and E. Segrè, *Ricerca sci.*, **9**, I, 638 (1938).

to exchange of hydrogen between hypophosphorous acid and water are in accord with the rate studies on oxidation of the hypophosphites, as discussed below.

Generally speaking, hypophosphorous acid and the hypophosphites are easily oxidized. Crystals of hypophosphorous acid are stable when stored[19] in the cold but, when impure, may slowly decompose at room temperature. Molten hypophosphorous acid and solutions of the acid decompose quite rapidly at temperatures greater than about 130°C., with the decomposition products being principally phosphine, phosphorous and phosphoric acids, and some hydrogen. Likewise, when strongly heated, the hypophosphite salts undergo decomposition to give phosphine, red phosphorus, phosphites, and phosphates—plus perhaps other products. This catastrophic decomposition into a number of products can rightfully be said to be an autoredox reaction. However, it should be noted that this reaction emphasizes the fact that the oxidation-reduction concept has no more applicability in the chemistry of phosphorus than it has in the chemistry of carbon (organic chemistry).

The kinetics of the reaction of hypophosphite ion with hydroxyl ion to form phosphite ion and gaseous hydrogen (see equation 7-8) has been studied.[16] The rate equation has been found to be

$$-d(H_2PO_2^-)/dt = k(H_2PO_2^-)(OH^-)^2 \qquad (7\text{-}10)$$

The rate constant, k, in this equation is approximately 3×10^{-4} min.$^{-1}$ at 100°C. It has been suggested that the form of the rate equation can best be explained by the following sequence of reactions in which the liberated hydrogen is believed to come from the hydroxyl ion, rather than from the hypophosphite.[15]

$$\begin{aligned} H_2PO_2^- + 2\,OH^- &\longrightarrow H_2PO_3^- + O^{2-} + H_2\uparrow \quad \text{(slow)} \\ O^{2-} + H_2O &\longrightarrow 2\,OH^- \quad \text{(rapid)} \end{aligned} \qquad (7\text{-}11)$$

Hypophosphites also decompose in neutral solutions at a reasonably rapid rate to give hydrogen when catalysts, such as platinum black, palladium, and copper, are employed.[16,42] These metals are readily precipitated in colloidal form from solutions of their salts by the action of sodium hypophosphite. The resulting colloidally dispersed metal then catalyzes the decomposition of the hypophosphite ion, so that hydrogen gas is evolved.

[42] A. Sieverts and E. Peters, *Z. physik. Chem.*, **91**, 199 (1916); A. Sieverts, *Z. anorg. Chem.*, **64**, 29 (1910); P. Breteau, *Bull. soc. chim. France*, **9**, 515 (1911); J. Bougault, *Compt. rend.*, **148**, 415 (1909); H. Wieland and W. Franke, *Bayr. Akad. Wissenschaften zu München, Ann.*, **464**, 101 (1928); also see P. Hersch, *J. Chem. Educ.*, **20**, 376 (1943).

These precipitated metals have also served as catalysts for reactions other than those involving the hypophosphite anion.[43] An isotope exchange study indicates that the evolution of hydrogen in neutral solutions of hypophosphites in the presence of metal catalysts occurs in such a manner that half of the hydrogen comes from the hypophosphite ion and half from the water (or from hydrogen or hydroxyl ions in the water or sorbed on the catalyst).[44] The data are in accord with the following chemical equation:

(7-12)

More detailed studies should be carried out on the mechanism of the decomposition of hypophosphite solutions, either catalyzed or uncatalyzed at various pH values.

The oxidation of hypophosphites by a number of different oxidizing agents, including the halogens, the halates, and various metal ions, has been the subject of a number of detailed kinetic studies. The main reaction, under the conditions of the investigations has been the conversion of the hypophosphite to phosphite. The subsequent reaction whereby phosphites are oxidized to phosphates is usually considerably slower in acid solution. The mechanism[45,46] of the oxidation of hypophosphite to phosphite by the halogens is shown by the following series of equations:

$$
\begin{aligned}
H_2PO_2^- + X_2 + H_2O &\longrightarrow H_3PO_3 + H^+ + 2\,X^- && \text{(slow, rate const. } = k_A\text{)}\\
H_2PO_2^- + H^+ &\rightleftharpoons (H_3PO_2)_I && \text{(rapid, reversible)}\\
(H_3PO_2)_I &\longrightarrow (H_3PO_2)_{II} && \text{(slow; rate const. } = k_1\text{)}\\
(H_3PO_2)_{II} &\longrightarrow (H_3PO_2)_I && \text{(moderately rapid; rate const. } = k_2\text{)}\\
(H_3PO_2)_{II} + X_2[\text{or } X_3^-] + H_2O &\longrightarrow H_3PO_3 + 2\,H^+ + 2\,X^- && \text{(rapid, rate const. } = k_3\text{)}
\end{aligned}
\qquad (7\text{-}13)
$$

With iodine the first reaction is so slow that k_A is essentially zero. The case of bromine is typical, and the rate equation corresponding to the reactions shown in equations 7-13 is given below.

$$-\,d(\Sigma H_3PO_2)/dt = k_{obs}\ (\Sigma H_3PO_2)(Br_2)$$

[43] P. Breteau, *Bull. soc. chim. France*, **9**, 518 (1911).

[44] W. Franke and J. Mönch, *Ann.*, **550**, 1 (1941).

[45] R. O. Griffith, A. McKeown, and R. P. Taylor, *Trans. Faraday Soc.*, **36**, 752 (1940) (iodine); R. O. Griffith and A. McKeown, *ibid.*, **30**, 530 (1934) (bromine and chlorine); A. D Mitchell, *J. Chem. Soc.*, **117**, 1322 (1920) (iodine); B. D. Steele, *J. Chem. Soc.*, **91**, 1641 (1908); *ibid.*, **92**, 1659 (1908) (iodine).

[46] P. Nylèn, *Z anorg. u. allgem. Chem.*, **230**, 385 (1937) (iodine).

where α is the degree of ionization of the H_3PO_2 and

$$k_{obs.} = k_A\alpha + \frac{k_3k_1(1 - \alpha)}{k_2 + k_3(\Sigma Br_2)} = k_4\alpha + \frac{k_1(1 - \alpha)}{(k_2/k_3) + (\Sigma Br_2)} \quad (7\text{-}14)$$

When the concentration of acid is low, α in equation 7-14 becomes approximately unity, so that the second term in the expression for $k_{obs.}$ is negligible. Under these conditions it is found that k_A is inversely proportional to $K + (Br^-)$, where K is the equilibrium constant for the decomposition of the tribromide ion

$$K = (Br_2)(Br^-)/(Br_3^-) \quad (7\text{-}15)$$

From this relationship it can be shown that, at higher values of the pH, the observed rate constant, k_{obs}, takes the following form

$$\lim_{\alpha \to 1} k_{obs} = (k_A/K)(\Sigma H_3PO_2)(Br_2) \quad (7\text{-}16)$$

At high acid concentrations, $k_A\alpha$ in equation 7-14 becomes very small, so that $k_{obs.}$ then equals the fraction involving k_1, k_2, and k_3. It is apparent from equation 7-14 that k_2 and k_3 cannot be evaluated separately—rather, the ratio k_2/k_3 is found. In experiments with added sulfuric acid, k_{obs} was found to vary only slightly with changes in the bromide ion concentration, so that both Br_2 and Br_3^- appear to react with the reactive form of hypophosphorous acid, $(H_3PO_2)_{II}$. It is concluded that HBrO is not the reactant, since the ratio k_2/k_3 is found to be directly and not inversely proportional to the acid concentration.

At unit concentration of the hydrogen ion, k_2/k_3 was found to be of the same order of magnitude for all three of the halogen atoms at the same temperature. Moreover, the temperature dependence is small. This indicates that the reaction between $(H_3PO_2)_{II}$ and the halogen takes place at every collision so that, at room temperature, k_3 is approximately equal to 4×10^{12}, with concentrations expressed in moles per liter and the time in minutes. This means that the equilibrium constant between the two forms of hypophosphorous acid can be evaluated. Since k_2/k_3 = about 10^{-2} min.$^{-1}$ and $k_1 = 0.21$ min.$^{-1}$, the equilibrium constant between the two forms is thus seen to be

$$K = (H_3PO_2)_{II}/(H_3PO_2)_I = k_1/k_2 \approx 10^{-12} \quad (7\text{-}17)$$

The rate of interchange between the two forms of hypophosphorous acid is found to be directly proportional to the hydrogen ion concentration and is the rate-determining process for the over-all oxidation reaction in acidic solution. Presumably, $(H_3PO_2)_I$ should be identified with the usual tautomeric modification in which there are two hydrogen atoms attached to the

phosphorus, and $(H_3PO_2)_{II}$ with the form in which two —OH groups are attached. It should be noted that, under equivalent conditions, the chlorine reaction is more rapid than the reaction with bromine, and the iodine reaction is the slowest of the three.

The kinetics of the oxidation of hypophosphorous acid by the iodate ion has been carefully studied,[47] and some work[48] has also been done on the slower reactions with bromate and chlorate. The kinetics of the original reaction between the iodate ion and hypophosphorous acid is closely related to the kinetics of the oxidation of hypophosphite with the halogens. However, there are a number of complicating side reactions such as the interaction between iodine and hypophosphorous acid and the reaction of phosphorous acid with iodine and iodate. When these interferences were eliminated, it was found that the rate-determining step in the reaction is again the conversion of $(H_3PO_2)_I$ to $(H_3PO_2)_{II}$. This was also found true in kinetic studies of the oxidation of hypophosphite with cupric salts[49] and with mercuric salts[50] in acid solution with moderate concentrations of the oxidizing agent.

For the oxidizing agents mentioned above and the others that have been studies,[51] it appears that the rate-determining step in acid media with moderate or large concentrations of the oxidant is always the conversion of $(H_3PO_2)_I$ to $(H_3PO_2)_{II}$. Under these conditions, it is found that the type or concentration of the oxidizing agent has essentially no effect on the rate, which becomes faster as the acidity is increased. The initial rate has the following form:

$$-d(H_3PO_2)/dt = k(H_3PO_2)(H^+) \qquad (7\text{-}18)$$

where a value of k equal to about 0.24 l./mole/min. is found for all of the various reactions studied.

[47] P. Hayward and D. M. Yost, *J. Am. Chem. Soc.*, **71**, 915 (1949) (iodate); V. Hovorka, *Collection Czechoslov. Chem. Comm.*, **2**, 559 (1930); *ibid.*, **2**, 609 (1930) (iodate); P. Neogi and B. Sen, *J. Indian Chem. Soc.*, **8**, 725 (1931) (iodate).

[48] B. Nath Sen, *Collection Czechoslov. Chem. Commun*, **10**, 321 (1938) (bromate); *Gazz. chim. ital.*, **78**, 423 (1948) (chlorate).

[49] A. D. Mitchell, *J. Chem. Soc.*, **121**, 1624 (1922); G. S. Vozdizhenskii and A. F. Gerasimov, *Trans. Butlerov Inst. Chem. Technol. Kazan*, **No. 1**, 108 (1934); P. Neogi and S. Mukerji, *J. Indian Chem. Soc.*, **6**, 529 (1929); J. E. Myers and J. B. Firth, *Z. anorg. Chem.*, **80**, 93 (1913).

[50] A. D. Mitchell, *J. Chem. Soc.*, **125**, 1013 (1924); *ibid.*, **119**, 1266 (1921); C. O. Gerfen, *Univ. Microfilms Pub. No. 2678*, Ann Arbor, Mich., 1951, 113 pp.

[51] A. D. Mitchell, *J. Chem. Soc.*, **125**, 564 (1924) (chromate ion); *ibid.*, **123**, 629 (1923) (silver ion); A. F. Bogoyavlenskii, *Uchenye Zapiski Kazan. Gosudarst Univ im. V. I. Ul'yanova-Lenina*, **100**, 69 (1940) (ferric ion); G. S. Vozdizhenskii and A. F Gerasimov, *J. Russ. Phys.-Chem. Soc.*, **62**, 409 (1930) (arsenate ion).

All of the kinetic work is in accord with the idea that the active form of hypophosphorous acid is present in extremely small amounts and that the rate of transition between the inactive and the active form is a slow process which, under easily realized experimental conditions, is the rate-determining step in the over-all reaction. These results agree with the nuclear magnetic resonance findings that 95% or more of the hypophosphite ion is present in the tautomer based on quadruply connected phosphorus. According to equation 7-17, there is only about one part per trillion of $HP(OH)_2$ in $H_2P(O)(OH)$!

Because the main commercial application for hypophosphites has been in the field of pharmaceuticals, their toxicity was studied quite carefully at the end of the 19th century.[52] There is no evidence that the hypophosphites exert the slightest toxic effect on mammals, and they pass through the mammalian system unchanged. Hypophosphites are rapidly eliminated from the system, primarily via the urine but also through the faeces.

A recently exploited application of hypophosphites is based on the reducing action of these compounds. Research,[53] primarily at the Bureau of Standards, has shown that nickel or cobalt or mixed alloys of nickel and cobalt can be chemically plated on metal surfaces by the hypophosphite ion to give hard, adherent coatings which are nonporous, even in a thin layer of less than one mil. Hypophosphites are also used in electroplating.[54] The reducing properties of hypophosphites may also find application in the manufacture of explosives.[55] For example, a mixture of equal parts of barium hypophosphite and potassium chlorate previously dried at 100°C. burns in the open air with great rapidity to produce a feeble report. When confined, this material gives a sharp detonation. The mixture is readily fired by an electric spark and is quite sensitive to shocks and friction. Likewise, a mixture of a syrupy solution of sodium hypophosphite and powdered sodium chlorate resembles nitroglycerin in some respects When a drop is heated on a metal surface, it boils, and finally, when quite dry, explodes with great violence

[52] M. Paquelin and L. Joly, *Compt. rend.*, **86**, 1505 (1878), *J. pharm. chim.*, **28**, 314 (1878); P. Schulz, *Arch. exp. Pathol.*, **18**, 174 (1884); G. Polk, *Pharm J.*, **5**, 425 (1874); T. Panzer, *Z. Untersuch. Nahr. u. Genussm.*, **5**, 11 (1902).

[53] A. Brenner and G. Riddell, *J. Research Natl. Bur. Standards*, **37**, 31 (1946); *ibid.*, **39**, 385 (1947); A. Brenner, D. E. Couch, and E. K. Williams, *ibid.*, **44**, 109 (1950); P. Talmey and W. J. Crehan, U. S. Pat. 2,658,839 (1957); E. Lamar Gostin, *Iron Age*, **171**, No. 24, 115 (1953); W. Blum, *Can. Metals*, **15**, No. 5, 52, 54 (1952).

[54] A. Brenner, D. E. Couch, and E. K. Williams, U. S. Pat. 2,643,221 (1953); T. H. Bonn and D. C. Wendell, Jr., U. S. Pat. 2,644,787 (1953).

[55] A. Berg and L. Cari-Mantraud, *Monit Sci.*, **14**, 271 (1893); *Bull. soc. chim. France*, **9**, 94 (1893).

Organic Derivatives of Hypophosphorous Acid—Phosphonous and Disubstituted Phosphinic Acids

One or both of the hydrogens attached directly to the phosphorus in hypophosphorous acid can be substituted by alkyl or aryl radicals. The well-known acids formed by substituting one hydrogen have been called alkanephosphonous or, more simply, phosphonous acids by Kosolapoff,[5] $RHP(O)(OH)$ The monoesters of this acid are little known, but there are a number of examples of the diester. The acids formed by substituting the two hydrogens attached directly to the phosphorus in hypophosphorous acid have been called dialkylphosphonic (or diarylphosphonic) or "secondary" phosphonic acids by Kosolapoff.[5] The free acids, $R_2P(O)(OH)$, and their esters, $R_2P(O)(OR)$, are well known.

Phosphonous acids, $R(H)P(O)(OH)$, are usually viscous oils in the aliphatic series but crystalline solids in the aromatic family. A common method of preparation[5,7] involves the air oxidation of primary phosphines, RPH_2. They are also often obtained from the hydrolysis of primary dihalophosphines, RPX_2. The dihalophosphines react smoothly with water to give a large yield of the corresponding phosphonous acid if the mixture is not allowed to reach unduly high temperatures. A reaction which shows the relation of the phosphonous acids to the parent acid—hypophosphorous acid—is the interaction between aldehydes or ketones and the hypophosphite ion.

$$RCHO + H_2P(O)(OH) \longrightarrow [RCH(OH)]PH(O)(OH) \qquad (7\text{-}19)$$

When larger proportions of the aldehyde or ketone are used, a considerable proportion of dialkylphosphinic acid is formed, viz

$$2\,RCHO + H_2P(O)(OH) \longrightarrow [RCH(OH)]_2P(O)(OH) \qquad (7\text{-}20)$$

The diesters of phosphonous acid, $RP(OR)_2$, especially of the aromatic phosphonous acids, are readily made by esterifying dihalophosphine, RPX_2, with the desired alcohol or phenol in the presence of the theoretical amount of a tertiary organic base, usually pyridine or dialkylaniline.[5,7] When dihalophosphines, RPX_2, are mixed with dry alcohols in the cold, the monoalkyl phosphonites, $RHP(O)(OR)$, result upon prolonged evacuation of the mixture. None of the monoesters has been well characterized. It should be noted that these esters cannot be made by the ordinary esterification methods used for synthesis of the esters of carboxylic acids.

Perhaps the best known of the phosphonous acids is phenylphosphonous acid,[56] also known as benzenephosphonous acid, $(C_6H_5)HP(O)(OH)$, which

[56] H. Kohler and A. Michaelis, *Ber.*, **10**, 807, 815, 816 (1877); G. X. Kamaĭ, *Zhur. Obshchet Khim.*, **18**, 443 (1948); and many others.

is a crystalline compound melting at 71°C. The dimethyl ester (b.p.$_{15\ mm}$ = 102°C., d_0^{20} = 1.085), the diethyl ester (b.p.$_{15\ mm}$ = 115°C., d_0^{20} = 1.025), the dipropyl ester (b.p.$_{15\ mm}$ = 137°C., d_0^{25} = 0.991), and the diphenyl ester (b.p.$_{15mm}$ = ca. 250°C., d_0 = 1.165), as well as several other esters of this acid have been made and characterized.[5] A fluorocarbon derivative of phosphonous acid has recently been described as the sodium salt,[57] Na $O_2(H)P(CF_3)$. The organic reactions of the phosphonous acids indicate that they exhibit the structure shown for them in Table 7-1 (item 6). These acids do not undergo many of the usual organic substitutions, as they are readily oxidized by such reagents as the halogens and nitric acid. Since the diesters exhibit triply connected phosphorus, $RP(OR)_2$, they have the ability to donate a pair of electrons. Adducts with electron acceptors such as cuprous chloride are known. Like the other esters based on triply connected phosphorus, the diesters of phosphonous acids readily undergo rearrangement when heated with alkyl halides,[58] carbon tetrachloride,[59] and certain other organic halogen-containing compounds,[7] viz.:

$$RP(OR')_2 + R''X \longrightarrow RR''P(O)(OR') + R'X \qquad (7\text{-}21)$$

Phenylphosphonous acid can be chlorinated but not with elemental chlorine,[60] which reacts violently to give a derivative believed to be based on two phosphorus atoms:

$$C_6H_5P(H)(O)(OH) + 2\,PCl_5 \longrightarrow C_6H_5P(O)(Cl_2) + POCl_3 + PCl_3 + 2\,HCl \qquad (7\text{-}22)$$

$$(C_6H_5)\overset{\overset{H}{|}}{\underset{\underset{O}{|}}{P}}OH + 2\,Cl_2 \longrightarrow (C_6H_5)\overset{\overset{O\ O}{|\ \ |}}{\underset{\underset{H\ H}{|\ \ |}}{P}}OP(C_6H_5) + C_6H_5PH_2 + 4\,HCl \qquad (7\text{-}23)$$

The thermal decomposition of phosphonous acids involves a transfer of ligands between several phosphorus atoms so that some of them become triply connected, being converted to organic phosphines.[61] The reaction is approximated by the following equation:

$$3\,RHP(O)(OH) \xrightarrow{\Delta} RPH_2 + 2\,RP(O)(OH)_2 \qquad (7\text{-}24)$$

[57] F. W. Bennett, H. J. Emeléus, and R. N. Hazeldine, *J. Chem. Soc.*, **1954**, 3598 3886.

[58] A. E. Arbusov, G. X. Kamal, and O. N. Belorossova, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 766 (1945); A. E. Arbusov and A. I. Razumov, *Bull. acad. sci. U.S.S R., Classe sci. chim.*, **1945**, 167; A. E. Arbusov and I. Arbusova, *J. Russ. Phys.-Chem. Soc.*, **61**, 1905 (1929).

[59] G. X. Kamal, *Compt. rend. acad. sci. U.S.S.R.*, **55**, 223 (1947).

[60] A. Michaelis, *Ann.*, **181**, 265 (1876).

[61] A. Michaelis, *Ann.*, **293**, 193, 261 (1896); *ibid.*, **294**, 1 (1897); *ibid.*, **181**, 265 (1876); A. Michaelis and J. Ananoff, *Ber.*, **7**, 1688 (1874); H. Kohler and A. Michaelis, *ibid.*, **10**, 807 (1877).

The disubstituted phosphinic acids, $R_2PO(OH)$, are often made by oxidation of phosphines—this time, secondary phosphines, R_2PH. The oxidation occurs rapidly in air, and isolation of possible intermediates of the structure R_2POH ("phosphinous" acids) appears to be impossible.[5] A common preparative method for the ester is via a Michaelis-Arbusov type of rearrangement[58] in which diesters of phosphonous acids react[58] with alkyl halides to give esters of disubstituted phosphinic acids, as was shown in equation 7-21. The lower members of the series of dialkylphosphinic acids are normally viscous liquids which freeze not far from room temperature, whereas the higher members and the aromatic-based acids are crystalline at normal temperatures. Examples are the dimethyl acid (hygroscopic, sublimable crystals, m.p. 76°C.) and the diethyl and dipropyl derivatives (both liquids at 25°C.). Diphenylphosphinic acid is a crystalline product, melting at 192°C. Its esters are also crystalline: ethyl ester, m.p. 165°C.; isopropyl ester, m.p. 96°C., isobutyl ester, m.p. 77°C.; and phenyl ester, m.p. 136°C. The bis(trifluoromethyl)phosphinic acid, $(CF_3)_2PO(OH)$, is said[62] to be the strongest known acid of phosphorus—having a dissociation constant greater than 10^{-1}. It is interesting to note that the heavy metal salts of the disubstituted phosphonic acids are appreciably soluble in polar organic solvents such as alcohol and ether. Interpretation of the heat of mixing with chloroform indicates that butyl dibutylphosphonate has a pronounced ability to combine with chloroform, presumably through hydrogen bonding.[63] The plasticizer and solvent action of the disubstituted phosphonite esters probably depends largely upon extensive secondary bonding of hydrogens to the isolated oxygen atom attached directly to the phosphorus.

Although no direct esterifications of disubstituted phosphinic acids, $R_2PO(OH)$, have been reported, esters have been made by converting the acid to its acid chloride[64] R_2POCl, through treatment with $SOCl_2$ or PCl_5, and then reacting with the proper alcohol. The methiodide of methyl methyl-*p*-dimethylaminophenylphosphinate has been resolved[65] into its optical isomers by fractional crystallization of the diasteroisomeric salts obtained by reaction with silver D(−)-dibenzoylhydrogentartrate. This

[62] H. J. Emeléus, R. N. Hazeldine, and Ram Chand Paul, *J. Chem. Soc.*, **1955**, 563.

[63] G. M. Kosolapoff and J. F. McCullough, *J. Am. Chem. Soc.*, **73**, 5392 (1951); J. F. McCullough, M.S. Thesis, University of Alabama, Auburn, Ala., 1951.

[64] C. J. Gibson and J. D. A. Johnson, *J. Chem. Soc.*, **1928**, 92; A. W. Hofmann, *Ber.*, **6**, 303 (1873).

[65] D. M. Coyne, W. E. McEwen, and C. A. Vander Werf, *J. Am. Chem. Soc.*, **78**, 3060 (1956).

represents the resolution of an ester of the type RR'P(O)(OR) having an unsymmetrical phosphorus atom.

Preparation and Structure of Phosphorous Acid, Its Salts and Esters

Orthophosphorous acid has the empirical formula, H_3PO_3. An acid having a hydrogen attached directly to the phosphorus, it can assume either of two tautomeric forms—as was the case for hypophosphorous acid. These two forms are $HP(O)(OH)_2$ and $P(OH)_3$. As will be pointed out later, it appears that all of the compounds of phosphorous acid except the triesters are predominantly in the form in which the phosphorus is quadruply connected, *i.e.*, $HP(O)(OH)_2$. Because of the existence of pyrophosphorous acid, which is discussed in a much later section of this chapter (under Acids Based on Several Phosphorus Atoms), the ortho prefix should be used with common phosphorous acid. However, in the remainder of this section, the prefix will be omitted, and the term "phosphorous acid" and "phosphites" will be used in referring to the ortho compounds.

Phosphorous acid is usually prepared by hydrolyzing phosphorus trichloride.[66] The reaction proceeds smoothly to give a reasonably pure product, except for dissolved hydrogen chloride which can be removed by heating the product under vacuum. The reaction is also readily carried out continuously. Additional purification of the phosphorous acid can be achieved by crystallization. As previously mentioned, phosphorous acid was first produced from slow oxidation of elemental phosphorus in a moist atmosphere. The oxidation of white phosphorus by moist air gives about 18% of the original phosphorus as phosphorous acid as compared to about 75% as phosphoric acid and 7% as all other oxyacids.[18] Phosphorous acid can also be made by treating its anhydride, P_4O_6, with water;[67] but this preparative method is never used because of the difficulty in preparing and isolating phosphorus trioxide (see Chapter 6). Extremely pure phosphorous acid can be made in aqueous solution by treating lead phosphite with hydrogen sulfide.[15] The lead phosphite is obtained in pure form by mixing solutions of recrystallized disodium phosphite with lead acetate. Alternatively, the recrystallized disodium phosphite can be converted directly to the acid by ion exchange. The primary and secondary salts of phos-

[66] D. Voigt and F. Gallais, *Inorganic Syntheses*, ed. J. C. Bailar, McGraw-Hill Book Co., York, 1953, Vol. IV, pp. 55–8; J. W. Lefforge and R. B. Hudson, U. S. Pat. 2,595,198–9 (1952); J. L. Krieger, U. S. Pat. 2,684,286 (1954); also T. Milobedzki and M. Friedman, *Chem. Polski*, **15**, 76 (1917); and many others.

[67] T. E. Thorpe and A. E. H. Tutton, *J. Chem. Soc.*, **57**, 545 (1890); *ibid.*, **59**, 1019 (1891); *Chem. News*, **61**, 212 (1890); *ibid.*, **64**, 304 (1891).

phorous acid are usually prepared from the acid made by hydrolyzing phosphorus trichloride. Purification of the salts is then achieved by recrystallization.

One of the most common methods of making esters of phosphorous acid is to react the appropriate alcohol with phosphorus trichloride.[5,7,68] When three or more moles of alcohol are employed per mole of phosphorus trichloride, the dialkyl phosphite and an alkyl halide are generally obtained.

$$3\,ROH + PCl_3 \longrightarrow (RO)_2PH(O) + RCl + 2\,HCl \qquad (7\text{-}25)$$

This reaction is usually carried out by adding the phosphorus trichloride to the agitated alcohol with cooling to moderate the reaction and to avoid scission of the product by the hydrogen chloride. Solvents such as carbon tetrachloride or benzene have been used occasionally but seem to offer no particular advantage. The hydrogen chloride and alkyl chloride are removed by evacuating the reaction vessel for several hours. Sometimes the hydrogen chloride is eliminated by saturating the reaction mixture with dry ammonia and then filtering off the resulting solid ammonium chloride prior to fractional vacuum distillation of the alkyl halide and dialkyl phosphite. It is usually said that the trialkyl ester is first formed and is later cleaved by the hydrogen chloride to give the alkyl chloride and the diester, as indicated in equation 7-25. However, this hypothetical mechanism has been questioned.[5] The over-all reaction requires two types of steps: (1) the replacement of chlorine by an alkoxy group, by which hydrogen chloride is liberated, and (2) a Michaelis-Arbusov rearrangement, which results in elimination of an alkyl chloride and conversion of triply connected phosphorus to quadruply connected phosphorus. A number of different mechanisms may be postulated for equation 7-25 which differ only with respect to the extent to which step 1 precedes or follows step 2. The dialkyl phosphite resulting from equation 7-25 is customarily purified by vacuum distillation.

The hydrochloric acid formed in equation 7-25 causes cleavage of the dialkyl phosphite. Indeed, the kinetics of this cleavage reaction has been measured,[69] and the activation energy for the diisopropyl phosphite cleavage is 21 kcal./mole. At elevated temperatures the reaction between three moles of alcohol and phosphorus trichloride is a classical preparation

[68] J. E. Malowan, *Inorganic Syntheses*, ed. J. C. Bailar McGraw-Hill Book Co., New York, 1953, Vol. IV, pp. 58–62; C. H. Campbell, D. H. Chadwick, and S. Kaufman, *Ind. Eng. Chem.*, **49**, 1871 (1957). For a discussion of the mechanism of this reaction, see A. N. Pudovik, *Doklady Akad. Nauk S.S.S.R.*, **84**, 519 (1952) and refs. 95, 96, 97, and 70.

[69] C. H. Campbell and D. H. Chadwick, *J. Am. Chem. Soc.*, **77**, 3379 (1955); W.

for alkyl halides (three moles of alkyl halide plus phosphorous acid). One method for obviating such a side reaction involving hydrogen chloride-cleavage of the dialkyl phosphite is to react the alcohol and phosphorus trichloride in a continuous system[68] under conditions where the hydrogen chloride is lost at once as a gas and the reaction heat is removed with the reaction products.

If three moles or more of alcohol are reacted with a mole of phosphorus trichloride in the presence of three moles of an organic base (such as pyridine or dimethylaniline), the reaction is forced to proceed to the point at which the tertiary ester of phosphorous acid is produced in good yield.

$$3\,ROH + PCl_3 + 3\,\text{[illegible]} \longrightarrow (RO)_3P + 3\,\text{[illegible]}\cdot HCl \qquad (7\text{-}26)$$

In carrying out this reaction, the phosphorus trichloride is added to a solution of the alcohol in an inert solvent such as ether or benzene containing an excess of the organic base. Adequate stirring and cooling to around 10°C. are used; and, after completion of the reaction, the organic ammonium halide ([illegible]·HCl) is filtered off, and the tertiary ester of phosphorous acid is purified by vacuum distillation. By reducing the amount of base to two moles, this reaction has also been used in the preparation of dialkyl phosphites.

Reaction of hydrogen chloride with the tertiary esters of phosphorous acid gives the diester plus the alkyl chloride. When an excess of phosphorus trichloride is reacted with an alcohol or phenol, the dichlorophosphite, $ROPCl_2$, is usually produced. This product can, in many cases, then be reacted with water to form the monoester of phosphorous acid. However, this reaction is often not a satisfactory preparative method for the monoalkyl phosphites because of continued hydrolysis to give phosphorous acid. In the aromatic series, the situation is worse, with the reaction generally failing because of easy hydrolysis of the monoester. In those cases where monaryl phosphites have been isolated from hydrolysis of the respective dichlorophosphite, only the theoretical amount of water was used, and the reaction was kept cold. Monoalkyl and aryl phosphites have also been made by hydrolysis of the higher esters. Thus, hydrolysis of dialkyl esters occurs very rapidly in alkaline solution - so rapidly in fact that the rate of hydrolysis of the lower members of the series cannot be accurately measured.

In much of the classical work on phosphite esters,[70] preparation was effected by reacting alkali alkoxides with phosphorus trihalides or halophos-

[70] A. E. Arbusov, *J. Russ. Phys.-Chem. Soc*, **38**, 161, 293, 687 (1906); also see A. E. Arbusov, *Uspekhi Khim.*, **20**, 521 (1951) for a review.

phites. However, this reaction is not much used today. When a mixture of phosphorous acid is warmed with alcohol, an equilibrium is established between these reactants and the respective monoalkyl phosphite, dialkyl phosphite, and water. Another synthesis which shows the relationship between phosphorous acid and its mono- and diesters is the reaction of metal phosphites with alkyl halides. This reaction has been employed in making a few dialkyl esters in poor yields by heating a mixture of lead phosphite with the desired alkyl iodide.

The salts of the monoesters of phosphorous acid are easily prepared; and, indeed, these esters are usually isolated in the form of their salts, which are made by simple neutralization with a base However, since the diesters are truly neutral in aqueous solution, their "salts" (or, more precisely, their metal derivatives) must be obtained by use of more drastic procedures, such as are employed in preparing the "salts" of alcohols. Thus, the alkali metal derivatives of the diesters of phosphorous acid are made by the direct action of the alkali metal or alkali metal alkoxide on the diester dissolved in a suitable solvent, such as ether, benzene, or hexane. The sodium compounds are very soluble in all organic solvents—even nonpolar ones, such as petroleum fractions when the ester groups are large (above butyl) Smaller ester groups lead to a diminution in the solubility.

Insoluble derivatives of the dialkyl phosphites have been made by simple metathesis reactions[71] in aqueous solution—with the driving force for the reaction being attributable to the insolubility of the product. Thus, the silver derivatives of the dialkyl phosphites are prepared by adding a theoretical amount of ammoniacal silver nitrate to an aqueous solution or suspension of the dialkyl phosphite, which is followed by careful neutralization with nitric acid. The silver "salt" can also be obtained by mixing the diester with silver nitrate in water and then gradually adding sodium or potassium hydroxide. The highly insoluble cuprous "salts" are made in a manner somewhat similar to the preparation of the silver "salts." They are obtained by adding hydrated cuprous oxide to an aqueous solution or suspension of the ester with shaking. The fibrous product is then skimmed from the surface.

Acetyl phosphite, $CH_3C(O)OPH(O)(OH)$, has been prepared by reacting acetyl chloride or acetic anhydride with phosphorous acid.[72] This compound has the properties of an acid anhydride.

[71] T. Milobedzki and M. Szwejkowska, *Chem. Polski*, **15**, 56 (1917). A. E. Arbusov, *Trudy Sessii Akad. Nauk, Org. Khim.*, **1939**, 211.

[72] B. T. Brooks, *J. Am. Chem. Soc.*, **34**, 492 (1912); U. Vvedenskii, *J. Russ. Phys-Chem. Soc.*, **20**, 29 (1888).

The Raman spectra of phosphorous acid and some of its salts and esters have been carefully studied.[27,73] The data for all but the triesters are in accord with a structure consisting of a distorted tetrahedron in which the phosphorus atom is connected to one hydrogen and three oxygen atoms. The P-H vibrations lead to intense lines at 2486 and 2509 cm.$^{-1}$. The nuclear magnetic resonance spectra[26] of phosphorus and hydrogen in all phosphites except the triesters are also in accord with one hydrogen being attached directly to the phosphorus, *e.g.*, see Figure 7-1. Thus, both the hydrogen and the phosphorus spectra of solutions of disodium phosphite exhibit two peaks, attributable to 1-1 spin-spin splitting. The phosphorus spectra of the free acid, its various soluble mono- and disubstituted salts, as well as its mono- and diesters, are the same as the spectrum of the disodium salt. However, as demonstrated in Figure 7-1, the triesters have a different phosphorus nuclear magnetic resonance spectrum in which only one major resonance peak occurs. This means that there is no hydrogen bonded directly to the phosphorus of the triesters, as would naturally be expected.

An x-ray structure study has been carried out[74] on magnesium phosphite hexahydrate, $MgO_3PH \cdot 6\ H_2O$. According to this study, the hydrogen and three oxygen atoms tetrahedrally surround the phosphorus atom of each discrete O_3PH^- group. The P-O atom-center distances equal 1.51 A., a value corresponding to about 0.6 π-bond per σ-bond. The crystals of $MgO_3PH \cdot 6\ H_2O$ are isomorphous with $MgSO_4 \cdot 6\ H_2O$, in which the placement of anions, cations, and water molecules are probably very similar. X-ray absorption spectra have been interpreted to show in which tautomeric form the various solid phosphites exist.[75,76] The position of the absorption edge of the *K*-line in the x-ray spectrum of phosphorus has been found to depend on the number and kind of atoms directly connected to the phosphorus. Thus, the absorption edge for triply connected phosphorus atoms lies near 5.77 A. and for the quadruply connected near 5.75 A. According to this work, it appears that phosphorous acid, its salts, and diethyl phosphite exist in the form in which the phosphorus is connected to four neighboring atoms. In addition, sodium diethyl phosphite in the solid state also seems to have the same structure, which means that the sodium

[73] R. Ananthakrishnan, *Nature*, **138**, 803 (1936); *Proc. Indian Acad. Sci.*, **5A**, 200 (1937); A. E. Arbusov, M. I. Batuev, and V. S. Vinogradova, *Compt. rend. acad. sci. U.R.S.S.*, **54**, 599 (1946).

[74] D. E. C. Corbridge, *Acta Cryst.*, **9**, 991 (1956).

[75] O. Stelling, *Z. anorg. u. allgem. Chem.*, **131**, 48 (1923); *Z. physik. Chem.*, **117**, 161, 194 (1925); Ph.D. Thesis, University of Lund, Lund, Sweden, 1927.

[76] P. Nylén, Ph.D. Thesis, University of Uppsala, Uppsala, Sweden, 1930.

would then be connected directly to the phosphorus, viz. $OP(Na)(OR)_2$. On the other hand, triphenyl phosphite is found to exist in the other tautomeric form, and this also appears to be the case for silver dialkyl phosphite—with the phosphorus being connected to only three neighboring atoms in both of these structures. The ultraviolet absorption spectra of phosphites have been interpreted in terms of structure,[77] and the conclusions are in accord with the other physical methods for distinguishing between the two tautomeric forms. Infrared data have also been reported for the phosphites.[28]

TABLE 7-4
Comparison of R_3PO_3 Isomers

Organic radicals, (R and R′)	Trialkyl phosphites, $P(OR)_3$	Dialkyl alkylphosphonates, $R'PO(OR)_2$
Trimethyl (CH_3—)	Oil, b p = 111 ± 1°C	Oil, b p = 181°C
	d_0^{20} = 1 0540	d_0^{20} = 1 1741
	n_D^{20} = 1 4095	n_D^{20} = 1 4105
Triethyl (CH_3CH_2—)	Oil, b p = 159°C	Oil, b p. = 198°C.
	d_0^{20} = 0 9687	d_0^{20} = 1 025
	n_D^{20} = 1 4134	n_D^{20} = 1 4164
Tri-*n*-propyl ($CH_3CH_2CH_2$—)	Oil, b.p $_{18\ mm}$ = ca 96°C	Oil, b p $_{18\ mm}$ = 126°C.
	d_0^{20} = 0 9522	d_0^{20} = 0 9776
	n_D^{20} = 1 4265	n_D^{20} = 1 4245
Tri-*n*-butyl ($CH_3CH_2CH_2CH_2$—)	Oil, b p.$_{20\ mm}$ = 130 ± 1°C.	Oil, b p.$_{20\ mm}$ = 161 ± 1°C
	d_0^{20} = 0 9257	d_0^{20} = 0 9427
	n_D^{19} = 1 4321	n_D^{25} = 1 4302
Tri-2-chloroethyl ($ClCH_2CH_2$—)	Oil, b p $_{2.5\ mm}$ = 113 ± 2°C	Crystals, m.p. = 37°C., b p $_{5\ mm}$ = 170°C
	d_0^{26} = 1 3453	d_0^{26} = 1.3906
	n_D^{26} = 1 4818	n_D^{26} = 1 4828
Diphenyl, 2-chloroethyl [the latter is R′ of $R'PO(OR)_2$] (C_6H_5—, $ClCH_2CH_2$—)	Oil, b p $_{2\ mm}$ = 157 ± 2°C	Oil, b p $_{2\ mm}$ = 189 ± 1°C
	d_0^{20} = 1 2347	d_0^{15} = 1 2671
	n_D^{20} = 1 5584	n_D^{15} = 1 5577
Triphenyl (C_6H_5—)	Crystals, m p. = 22°C	Crystals, m.p. = 69 ± 5°C.

All of the physical data are in accord with the idea that the trialkyl phosphites are based on triply connected phosphorus and thus have the structure $P(OR)_3$. In Table 7-4 the physical properties of some trialkyl phosphites, $P(OR)_3$, are compared with the isomeric dialkyl alkylphosphonates,

[77] J. L. de Hauss, *Chim. anal.*, **34**, 248 (1952); Sh. N. Ali, *Indian J. Phys.*, **13**, 309 (1939); T. Milobedzki and W. Borowski, *Roczniki Chem.*, **18**, 725 (1938).

$RPO(OR)_2$, to show that these two types of compounds have indeed different properties and hence different structures. The isomers in which the phosphorus is triply connected to its neighboring atoms are found to have uniformly lower boiling points, densities, and indices of refraction—with the differences in density and index of refraction becoming less pronounced as the molecular weight of the organic parts of the molecule is increased. It is interesting to note that, although $(CH_3O)_3P$ is only slightly soluble in water, $(CH_3O)_2PHO$—as well as $(C_2H_5O)_2PHO$– is miscible. The nonbridging oxygen in the compounds based on the tetrahedrally connected phosphorus is probably strongly hydrogen bonded to the water molecules.

Considerable space in the literature has been devoted to chemical "proofs" that particular phosphites are predominantly present in one or the other tautomeric form. Much of this literature has been reviewed by Nylén.[76] Probably the most elegant attack on this problem was instituted by Arbusov,[70] who clarified much of the earlier work and used the formation of addition compounds with cuprous halides to demonstrate which phosphites were based on triply connected phosphorus atoms. Arbusov's results agree with those of the physical studies reported above. It is interesting to note that the interpretation of chemical reaction data both for and against a given tautomeric modification is still going strong,[78] although present-day theory indicates that the structure of a reaction product is determined by the activated complex which is usually present in the reactants only in infinitesimally small amounts and may have a considerably different structure

Physical Properties and Reactions of Phosphorous Acid, Its Salts and Esters

Pure orthophosphorous acid is a colorless, deliquescent solid melting at 70.1°C. The crystalline acid[30] has a specific gravity of 1.65 at 21°C. Its heat of fusion is 3.07 kcal./mole, and the heat of solution in an excess of water is −0.13 kcal./mole. The solubility[79] of the acid in water is presented as a function of temperature in Figure 7-3. The melting point curve of

[78] J. H. Kolitowska, *Roczniki Chem.*, **27**, 191 (1953) (In this paper it is stated that mild oxidants convert the "enol" form of phosphorous acid into hypophosphoric acid, whereas under the same conditions the "keto" form is converted into phosphoric acid.); J. Sperber and J. F. Bodmer, *Ber.*, **69B**, 974 (1936) (These authors believe that free phosphorous acid is based on triply connected phosphorus!); also see D. Voigt, *Bull. soc. chim. France*, **1953**, 212, who attempted to prepare the form of phosphorous acid having the formula, $P(OH)_3$.

[79] A. Italiener, *Beitrage zur Kenntnis der phosphorigen Saure und ihrer Salze*, Freiburg im Breisgau, Germany, 1917. Because of several inconsistencies which are apparent in these data, the BaO-P_2O_3-H_2O phase diagram obtained by Italienier is not given here.

mixtures of phosphorous and phosphoric acids has been determined,[80] and it was shown that there is a simple eutectic occurring at −14°C. and 37 mole-% phosphorous acid. A simple eutectic is also found in the system dioxane–phosphorous acid.[81]

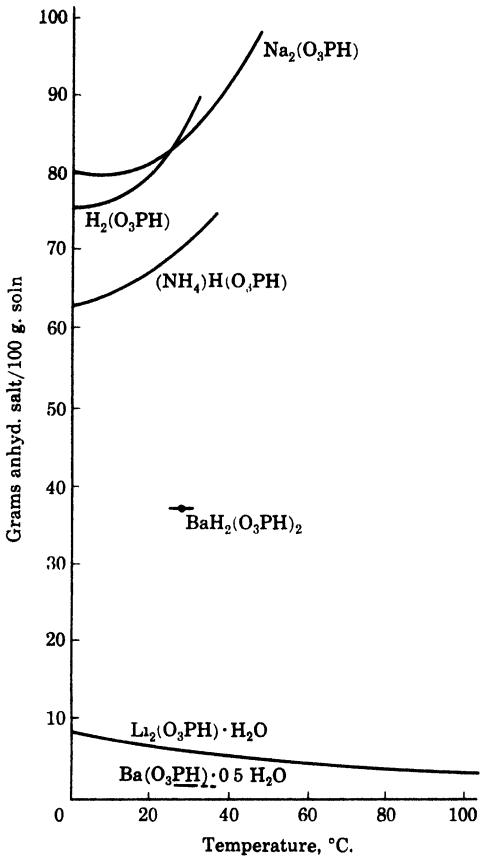


Fig. 7-3. The solubility of a number of phosphites as a function of temperature.

Phosphorous acid is a dibasic acid and, in spite of the attempt of early workers[20] to make a trisubstituted salt, only mono- and disubstituted salts

[80] A. Rosenheim, W. Stadler, and F. Jacobsohn, *Ber.*, **39**, 2837 (1906).
[81] Ya. P. Mezhennïĭ, *Zhur. Obshchei Khim.*, **19**, 404 (1949).

are formed. The first ionization constant[31,76,82] at 18°C. is 5.1×10^{-2} as recalculated from Kolthoff's data, using the Shedlovsky function. The second ionization constant at 18°C. is 1.8×10^{-7}. As might be expected, phosphorus atoms do not exchange[41,83] between phosphorous acid and the other oxyacids of phosphorus.

Two crystalline ammonium phosphites are known,[20] $(NH_4)H(O_3PH)$ and $(NH_4)_2O_3PH \cdot H_2O$. Both of these salts are quite deliquescent and very soluble in water. Upon heating them, ammonia is lost at first, followed by decomposition of the resulting ammoniated phosphorous acid into phosphine and other products. The normal lithium salt of phosphorous acid, $Li_2O_3PH \cdot H_2O$, is probably the most insoluble of the alkali metal phosphites, as shown in Figure 7-3, whereas the acid salt, $LiH(O_3PH)$, is quite soluble in water. The series of sodium and potassium salts of phosphorous acid which have been described are listed here: $Na_2H_4(O_3PH)_3 \cdot 0.5\ H_2O$, $NaH(O_3PH) \cdot 2.5\ H_2O$, $Na_2O_3PH \cdot 5\ H_2O$, $K_2H_4(O_3PH)_3$, $KH(O_3PH)$, and K_2O_3PH. With respect to the solubility of its salts, phosphorous acid is more similar to phosphoric acid than it is to hypophosphorous acid. Thus, the alkaline earth metal salts of phosphorous acid, as well as the phosphites of heavy metals are generally relatively insoluble as compared to the alkali metal phosphites. The solubility characteristics of the barium phosphites have been measured[79] as a function of $Ba(OH)_2$ and $H_2(O_3PH)$ concentrations at 30°C.

Phosphorous acid and its salts undergo decomposition when heated. The reaction products are said to be primarily phosphine and phosphates in the absence of water, and hydrogen plus phosphates in the presence of water. However, other products, including red phosphorus, are also usually formed so that a whole spectrum of decomposition products can result under the proper conditions. The equations usually given[84] for the thermal decomposition of the acid are

$$4\ H_2(O_3PH) \xrightarrow{\Delta} 3\ H_3PO_4 + PH_3 \uparrow \qquad (7\text{-}27)$$

$$H_2(O_3PH) + H_2O \xrightarrow{\Delta} H_3PO_4 + H_2 \uparrow \qquad (7\text{-}28)$$

[82] K. Takahasi and N. Yui, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **20**, 521 (1941); E. Blanc, *J. chim. phys.*, **18**, 28 (1920); T. Milobedzki and K. Boratynski, *Roczniki Chem.*, **8**, 554 (1928). Also see W. Ostwald, *Z. physik. Chem.*, **3**, 170, 241, 369 (1889) and A. Italiener in ref. 79 for pertinent conductivity data. The conductivity in the presence of some organic acids is reported by P. Kohler, *Arch. sci. phys. et nat.*, **26**, 157 (1944); R. Duckert, P. Kohler, and P. Wenger, *Helv. Chim. Acta*, **26**, 2026 (1943).

[83] J. N. Wilson, *J. Am. Chem. Soc.*, **60**, 2697 (1938).

[84] L. Hackspill and J. Weiss, *Chemie & industrie, Special No.*, 453 (March, 1932).

These reactions are fairly rapid at temperatures around about 250–275°C., and kinetic data have been reported.[84] Unlike the hypophosphites, the phosphites do not react with concentrated sodium hydroxide solutions to give hydrogen upon heating.

The kinetics of the oxidation of the phosphite to the phosphate ion by halogens,[85] mercuric chloride,[86] and other oxidizing agents[87] have been investigated in aqueous solution. In the reactions both with mercuric chloride and with iodine, Mitchell postulated that the rate-determining step is the transition between an inactive (presumably $HP(O)(OH)_2$) and an active (presumably $P(OH)_3$) form of phosphorous acid. In doing this, he drew a strong parallel between the oxidation of the phosphite anion and that of the hypophosphite anion, described in equations 7-13–7-18. However, it should be noted that Berthoud and Berger did not need this mechanism to explain their data on the iodine reaction nor was it employed in the mechanism derived for the bromine reaction. This has been recently discussed by Yost and Russell,[15] who also reviewed the kinetics of the reaction with mercuric chloride and postulated a rather unbelievable mechanism for this latter reaction. Obviously, considerably more effort is needed before the kinetics of the oxidation of the phosphite ion is properly understood. However, the available data show that a chain mechanism or, at least, several competing steps must be assumed for most cases.

The important thing to remember is that the phosphite ion is a strong reducing agent which reacts very slowly and in a rather complex manner with various oxidizing agents. Its oxidation potential is estimated[88] to be 0.28 v. in acidic solution and 1.12 v. in alkaline solution. It should be noted that these values are close to those estimated for the oxidation of the formate ion to carbon dioxide in acidic solution (0.20 v.) and to the carbonate ion in alkaline solution (1.01 v.). The autoredox decomposition of phosphites on heating is also reasonably similar to that observed when formates or, say, oxalates are heated. As will be more readily apparent

[85] A. D. Mitchell, *J. Chem. Soc.*, **123**, 2241 (1923); A. Berthoud and W. E. Berger, *J. chim. phys.*, **25**, 568 (1928) (iodine); R. O. Griffith and A. McKeown, *Trans. Faraday Soc.*, **29**, 611 (1933) (bromine and chlorine).

[86] A. D. Mitchell, *J. Chem. Soc.*, **125**, 1013 (1924); G. A. Linhart, *Am. J. Sci.*, **35**, 353 (1913); J. B. Garner, J. E. Foglesong and R. Wilson, *Am. Chem. J.*, **46**, 361 (1912).

[87] N. R. Dhar, *Ann. chim.*, **11**, 130 (1919); B. Kirson, *Bull. soc. chim. France*, **1948**, 521 (chromates); S. S. Bhatnagar, R. N. Mathur, and R. N. Kapur, *Phil. Mag.*, **8**, 457 (1929) (effect of magnetic fields on the chromate reaction); B. Blaser, *Z. physik. Chem.*, **A166**, 64 (1933) (catalysis of reaction with silver ion); E. H. Riesenfeld and T. L. Chang, *Z. anorg. u. allgem. Chem.*, **230**, 239 (1937) ($KMnO_4$); and others.

[88] W. M. Latimer, *Oxidation Potentials*, 2nd ed., Prentice-Hall Inc., New York, 1952, pp. 107, 130–34.

from the latter part of this chapter, where the lower oxyacids based on several phosphorus atoms are discussed, the chemistry of the lower oxyacids of phosphorus is quite closely related to the chemistry of the organic acids.

The phosphites exhibit considerable toxicity,[89] acting on the nerve centers and abdominal glands.

A peroxy derivative of phosphorous acid has been said to have been made by treating sodium hypophosphite solutions with ozone.[90] This peroxy acid has been assigned the formula HP(O)(OOH)(OH).

The monoalkyl and monoaryl phosphites are generally known as their crystalline salts. The sodium and ammonium salts are usually water soluble, whereas the alkaline earth metal and ferric salts are poorly soluble in water. It is generally stated that the free acid esters are unstable oils,[5,7] which presumably means that they decompose to give unesterified phosphorous acid plus its diester. The acid dissociation constant of monoethyl phosphite has been measured[34] and is found to be 1.6×10^{-1} at 20°C., which means that it is a considerably stronger acid than is the strongest acid hydrogen of unesterified phosphorous acid.

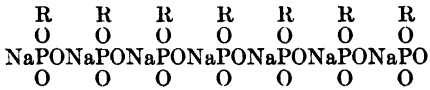
The monoalkyl or monoaryl phosphites, $H^+[HPO_2(OR)]^-$, are isomeric with the alkyl- or arylphosphonic acids, $2\,H^+ + (RPO_3)^{2-}$, since both types of compounds exhibit the same empirical formula, H_2RPO_3. As there is a consistent difference in properties between the two types of compounds, it is certain that they are different. Thus, the monoalkyl phosphites are unstable oils, whereas the isomeric alkylphosphonic acids are crystalline solids exhibiting moderately high melting points; *e.g.*, for $CH_3PO(OH)_2$, the m.p. is 105°C.

The dialkyl or diaryl phosphites are essentially odorless liquids (or low-melting solids, in the case of higher members) which can be vacuum distilled. In water they exhibit no buffering capacity and are neutral in the usual sense of the word, in that they do not form salts with bases. This behavior is of course to be expected from their accepted structure in which the hydrogen is attached directly to the phosphorus and hence is not an acidic hydrogen. Both the primary and secondary esters of phosphorous acid are quite resistant to oxidation. In spite of their neutral behavior, it is, however, possible to make metal derivatives of the secondary esters of phosphorous acid, as has been previously discussed. A recent study has shown that the sodium derivatives of the diesters of phosphorous acid are strongly associated when dissolved in organic solvents to give agglomerates

[89] P. Schulz, *Arch. Exp. Pathol. Pharmakol.*, **23**, 150 (1887).

[90] W. Bockemuller and T. Gotz, *Ann.*, **508**, 263 (1934).

of extremely high molecular weight.[91,92] It is interesting to note that these solutions foam and suds in a manner similar to aqueous solutions of surfactants. To explain these findings, Isbell has postulated the formation of very long-chain association polymers in the organic solvents, as indicated below:



(7-29)

It is to be presumed that the sodium is primarily ionic in these structures, although it may exhibit some *sp*-bonding. These agglomerates (postulated as chains) are probably quite equivalent to the micelles which organic surfactants form in aqueous solution. However, in this case it is the sodium which acts as the lyophobic constituent in the structure. From the small amount of available data, which are not truly comparative, it appears that the sodium derivative of the dialkyl phosphites is more strongly associated in nonpolar solvents than is the hydrogen derivative[63] in polar solvents This is probably attributable to the fact that the hydrogen is very firmly bonded to the phosphorus, as evidenced by the nuclear magnetic resonance measurements,[26] so that the type of strong hydrogen bonding in which a readily exchangeable hydrogen is rather equally shared between its neighboring atoms does not exist. The kinetics[93] of the reaction between the sodium derivative of dibutyl phosphite and butyl bromide also supports the idea of considerable association of the sodium derivative.

The tertiary phosphite esters are perhaps the most reactive of the compounds classed as phosphites. Because of their unshared pair of electrons, they form a number of addition compounds[7,70] with such substances as CuCl, $PdCl_2$, $PtCl_2$, $PtCl_4$, AuCl, and $HgCl_2$. It is interesting to note that complexes of the trialkyl phosphites with metal salts of phenols, amides, and other organic compounds have been prepared for use as antiknock additives in gasoline.[94] The tertiary phosphite esters also react readily

[91] A. F. Isbell, Paper presented at the *Phosphorus Symposium, 129th Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1956.* Also see R. B. Fox and D. L. Venezky, *Naval Res. Lab. Rept. 4806*, 1 (1956) (PB No. 121210) for some recent related studies.

[92] For earlier work on these compounds, see T. Milobedzki, *Roczniki Chem.*, **4**, 183 (1924); *Chem. Polski*, **15**, 89 (1917); *Ber.*, **45**, 298 (1912); and ref. 71.

[93] J. H. Shaffer, M.S. Thesis, Texas A. and M. College, College Station, Texas, 1955 (under the direction of A. F. Isbell).

[94] A. J. van Peski and J. A. van Melsen, U. S. Pat. 2,150,349 (1939); N. V. Bataafsche Petroleum Maatschappij, Brit. Pat. 477,673 (1937).

with oxygen or sulfur to give the respective phosphates or thiophosphates, *e.g.*

$$2\,(RO)_3P + O_2 \longrightarrow 2\,(RO)_3PO \qquad (7\text{-}30)$$

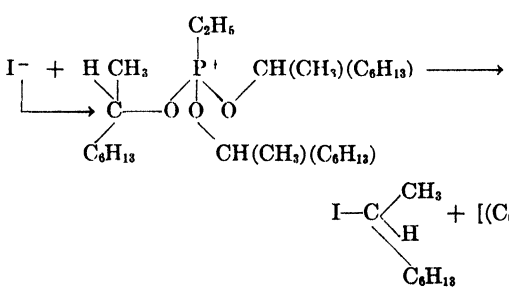
Perhaps the most interesting reaction of the tertiary phosphite esters is the Michaelis-Arbusov rearrangement,[58,92,95] the equation of which is given below.

$$P(OR)_3 + R'X \rightleftharpoons \underset{\text{activated complex}}{[(RO)_3R'OX]} \cdots \rightarrow R'PO(OR)_2 + RX \qquad (7\text{-}31)$$

A variation of this reaction is observed with the sodium derivative of the diester.

$$Na[OP(OR)_2] + R'X \longrightarrow R'PO(OR)_2 + NaX\downarrow \qquad (7\text{-}32)$$

The phosphonium intermediate shown in brackets in equation 7-31 has been isolated in the case of the reaction between triphenyl phosphite and methyl iodide.[96] This isolated intermediate, $(C_6H_5O)_3CH_3PI$, is easily decomposed by water into C_6H_5OH, HI, and $CH_3PO(OC_6H_5)_2$. When the phosphite reacting in the Michaelis-Arbusov rearrangement was the ester of an optically active alcohol, it was found that optical inversion takes place during the formation of the organic halide.[97] This study was carried out by reacting tri-(+)-octan-2-ol phosphite with methyl iodide to get (−)-2-iodooctane. These results imply that the halide of the assumed phosphonium intermediate approaches the ester-carbon on the opposite side from the oxygen of the C—O—P linkage to give a kind of Walden inversion, as shown in the following equation.



$$+\ [(C_6H_{13})(CH_3)HCO]_2PO(C_2H_5) \qquad (7\text{-}33)$$

[95] A. E. Arbusov, M.S. Thesis, University of New Alexandria, Russia, 1905; Ph.D. Thesis, University of Kazan, Russia, 1914; *J. Russ. Phys.-Chem. Soc.*, **38**, 687 (1906). For a more recent work, also see G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67**, 1180 (1945).

[96] A. Michaelis and R. Kähne, *Ber.*, **31**, 1048 (1898).

[97] W. Gerrard and W. J. Green, *J. Chem. Soc.*, **1951**, 2550; W. Gerrard, *ibid.*, **1944**, 85.

It should be noted that the Michaelis-Arbusov rearrangement occurs not only with simple alkyl halides but with organic polyhalides, such as methylene bromide or carbon tetrachloride,[59] haloethers, haloketones, and halocarboxylic acids and their derivatives There are, of course, some exceptions to this broad generality,[7] such as the oxidation of triethyl phosphite by nitromethyl bromide.[98] If, in equation 7-31, the radical R′ is identical to

$$2\,BrCH_2NO_2 + 2\,(C_2H_5O)_3P \longrightarrow (C_2H_5O)_3PO + 2\,NO + C_2H_4 + (C_2H_5O)_3PBr_2 \quad (7\text{-}34)$$

the radical R, the reaction becomes a true isomerization, and only trace amounts of the alkyl halide are needed in the reaction since the alkyl halide is continuously regenerated and hence merely serves as a catalyst.

An interesting form of the Michaelis-Arbusov rearrangement is found in the series of tri-2-haloethyl phosphites, $(XCH_2CH_2O)_3P$, which undergo the isomerism spontaneously on heating;[99] as both the alkyl halide and the ester required by equation 7-31 are present in the same molecule. The major product from the isomerism is, in this case, $XCH_2CH_2PO(OCH_2CH_2X)_2$. There are also some byproducts

Ester interchange between phosphites exhibiting different organic groups is well known.[100] This behavior of phosphite esters should be compared with the practically undetectably slow rate of interchange of phosphate esters, discussed on p. 584. Presumably, the difference in rate is due to the fact that the dynamic equilibrium between the form based on quadruply connected phosphorus and the form based on triply connected phosphorus in the phosphites affords a mechanism for exchange which is not present in the phosphates.

Phosphonic Acids and Their Esters

The hydrogen attached directly to the phosphorus in phosphorous acid can be substituted by an alkyl or aryl radical to give the organic acids which Kosolapoff calls alkanephosphonic acids. These acids and their esters are very well known, and a large number of examples, based on various organic radicals, have been made and characterized. The Michaelis-Arbusov rear-

[98] A. E. Arbusov, B. A Arbusov, and B P. Lugovkin, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1947**, 535.

[99] M. I. Kabachnik and P. A. Rossiĭskaya, *Izvest. Akad. Nauk S.S.S.R, Otdel. Khim. Nauk*, **1946**, 295, 403, 515.

[100] D. H. Chadwick, P. Sanguinetti, and E. E. Hardy, *Abstracts of Papers Presented at 122nd National Meeting of the American Chemical Society, Atlantic City, Sept. 14–19, 1952;* also private communication from D. H. Chadwick; F. W. Hoffmann, R. J. Ess, and R. P. Usinger, *J. Am. Chem. Soc.*, **78**, 5817 (1956).

rangement described in equation 7-31 is a good method for preparing the esters. The acids are often made by oxidation of the equivalent primary phosphine, RPH_2, using such oxidizing agents as nitric acid, potassium permanganate, or sodium dichromate. As was pointed out previously, simple air oxidation leads to the phosphonous acid, $RHPO(OH)$, instead of the monosubstituted phosphonic acid, $RPO(OH)_2$, obtained with stronger oxidizing agents. Obviously, phosphonous acids can be further oxidized to the monosubstituted phosphonic acids.

These phosphonic acids are usually obtained in the form of well-crystallized solids having melting points lying between 100 and about 200°C Thus, $CH_3PO(OH)_2$ melts at 105°C., $C_6H_5PO(OH)_2$ melts at 159°C., and $4\text{-}(C_6H_5CH_2CH_2)C_6H_4PO(OH)_2$ melts at 256°C. On the other hand, the lower aliphatic esters of these acids are oils which can be distilled under reduced pressure. The aromatic esters, however, are crystals which melt at considerably lower temperatures (say, about 50°C lower) than do the acids.

The monosubstituted phosphonic acids, $RPO(OH)_2$, are dibasic, with the first ionization constant being in the neighborhood of 10^{-2} and the second being near 10^{-8}. However, the fluorocarbon derivative, $(CF_3)PO(OH)_2$ is a stronger acid,[57] for which $K_1 = 7 \times 10^{-2}$ and $K_2 = 1.2 \times 10^{-4}$. The dissociation constants of several of these acids are given[5,76,101] in Table 7-3.

The ultraviolet absorption spectra[102] of some benzenephosphonic acids have been interpreted to show that there is essentially no coupling between the π-bonding in the benzene ring and that associated with the phosphorus atom. Generally, when there is considerable resonance between a radical attached to a benzene ring and the ring itself, there is a marked difference in the ultraviolet absorption spectrum from that of unsubstituted benzene. However, the absorption spectra of benzene and phenylphosphonic acid in the range from 240 to 280 mμ exhibit the same shape, with the spectrum of the phosphorus compound being shifted about 10 mμ to higher wave lengths. Moreover, the benzene spectrum of $(C_6H_5)_2PO(OH)$ is almost identical to that of $C_6H_5PO(OH)_2$. This indicates that the multiple bonds resonating around the phosphorus atom interact only slightly or not at all with the resonating multiple bonds within the phenyl group.

Nuclear magnetic resonance studies of the phosphonic acids and

[101] H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953); *ibid.*, **76**, 1548 (1954) give classical dissociation constants for benzenephosphonic acids; also see L. D. Freedman and H. H. Jaffé, *ibid*, **77**, 920 (1955).

[102] H. H. Jaffé and L. D. Freedman, *J Am. Chem. Soc*, **74**, 1069 (1952); also see H. H. Jaffé, *J. Chem. Phys*, **22**, 1430 (1954)

their esters offer a direct way to measure the relative electron-donating ability of the organic radicals attached directly to the phosphorus.[26] The measured chemical shifts of the phosphorus nuclear magnetic resonance peaks as compared to that of 85% phosphoric acid are shown in Figure 7-4, from which it can be seen that the stronger electron-donating groups lead to lesser magnetic shielding of the phosphorus nucleus. The order in which

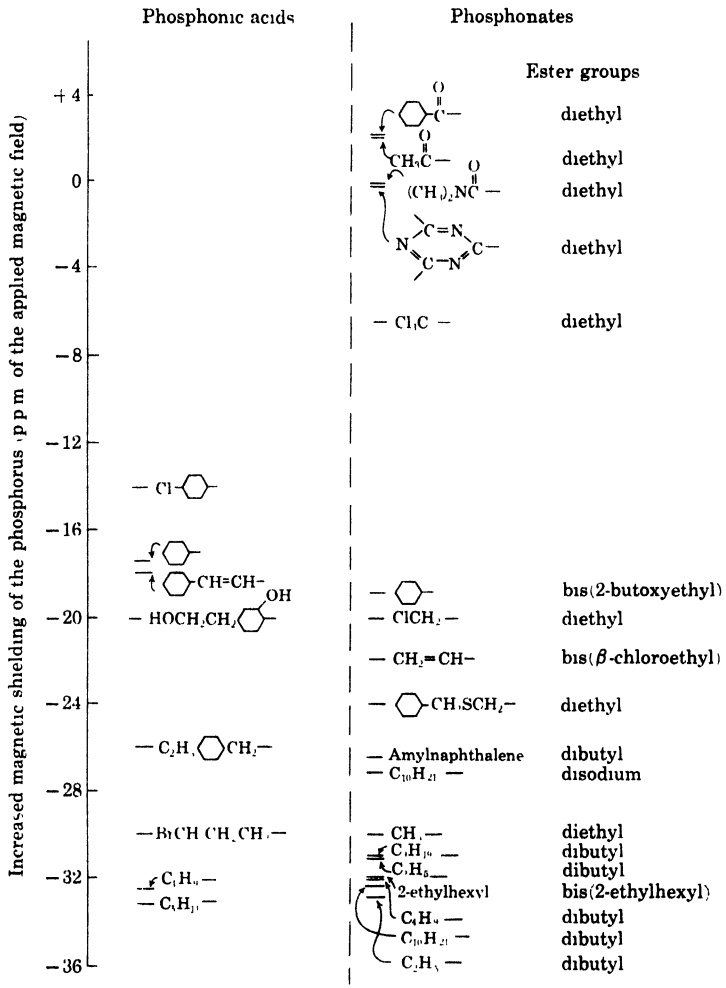


Fig. 7-4 P^{32} nuclear magnetic resonance shifts due to various substituents attached directly to the phosphorus in phosphonic acids and their esters

the radicals are listed in Figure 7-4 follows the accepted series[103] given for inductive effects in the case of those radicals which have been studied by other techniques—with the single exception of hydrogen.

Nomenclature

One of the most confused areas of nomenclature in the active fields of present-day chemistry consists of the organic lower oxyacids of phosphorus. As pointed out in Table 7-1 (item 9), the compound $R_2PO(OH)$ is called dialkylphosphinic acid in *Chemical Abstracts*, dialkylphosphonic acid in Kosolapoff's book,[5] dialkylphosphonous acid according to British usage before 1952, and dialkylphosphinous acid in Beilstein. To top this off, I have pointed out in the preceding text that this acid is indeed a derivative of hypophosphorous acid, so that it could be named dialkylhypophosphorous acid!

Special committees were set up a few years ago in the United States and in England to resolve the problem of naming phosphorus compounds based on a single phosphorus atom. The reports of these committees, who met together and came to general agreement, were issued in 1952.[104] In trying to set up a system of nomenclature for as yet undiscovered acids based on phosphorus, the committees assumed that phosphorus was either "trivalent" or "quinquevalent" and then came up with the following list of acids, most of which they realized were hypothetical.

Trivalent Acids		(7-35)
Phosphorous acid	$(HO)_3P$	
Phosphonous acid	$HP(OH)_2$	
Phosphinous acid	$H_2P \cdot OH$	
Phosphenous acid	$HO \cdot PO$	
Quinquevalent Acids		**(7-36)**
Phosphoric acid	$(HO)_3PO$	
Phosphonic acid	$HPO(OH)_2$	
Phosphinic acid	$H_2PO \cdot OH$	
Phosphenic acid	$HO \cdot PO(O)$	
Phosphoranoic acid	$H_4P \cdot OH$	
Phosphoranedioic acid	$H_3P(OH)_2$	
Phosphoranetrioic acid	$H_2P(OH)_3$	
Phosphoranetetroic acid	$HP(OH)_4$	
Phosphoranepentoic acid	$(HO)_5P$	

[103] H. Gilman, *Organic Chemistry, An Advanced Treatise*, 2nd ed., John Wiley & Sons, Inc., New York, Vol II, Chapt. 25.

[104] A. M. Patterson, *Chem. Eng. News*, **30**, 2336 (1952); L. R. Drake *et al.*, *ibid.*, **30**, 4515 (1952); Anon., *J. Chem. Soc.*, **1952**, 5122.

It is obvious from the tone of the committees' reports, as well as from some of the absurd acids listed above, that no consideration was given to the natural regularities and systematic behavior which is to be found in the chemistry of phosphorus and its compounds. Instead, the approach was wholly empirical, following outmoded classical reasoning. If the systematic approach to phosphorus chemistry presented in this book has any meaning, it is quite obvious that search for a "phosphenous acid," with the formula HOPO, or for any of its derivatives would have to be made in band spectra, since compounds having such structures are unstable under normal conditions. In addition to use of an obsolete, wholly empirical approach, the nomenclature committees are also to be criticized for bringing even more confusion into an already confused field. This point has been made by some Swedish authors,[105] who in addition suggested their own system of names.

The confusion lies in the endings -inous, -inic, -onous, and -onic and can be completely overcome by discarding these suffixes entirely. By naming the organic acids of phosphorus as derivatives of the well-known inorganic acids, the names of which have been generally accepted for many decades, a logical system of nomenclature which applies equally well to the inorganic acids and all of the organic ones is obtained.

The system of nomenclature recommended by the 1952 American and British committees has a serious disadvantage in that the hypophosphorous acid is called phosphinic acid with respect to its esters, and phosphorous acid is called phosphonic acid with respect to its esters. The committee recommends retaining the names hypophosphorous and phosphorous for the inorganic acids, so that the name changes when the acid is esterified!

This system of naming is applied in the next to the last column of Table 7-1. It has the advantage that the confusing suffixes -inous, -inic, -onous, and -onic are done away with. This idea of naming all of the organic acids as derivatives of the well-known inorganic acids has in part occasionally appeared in the literature.[106] Although it is strongly recommended that the four suffixes usually employed in naming the organic derivatives of hypophosphorous and phosphorous acids be discontinued because of the confusion associated with their use, they have been employed in this text in order to make it consistent with the forthcoming second edition of the book by Kosolapoff.[5]

The coordination-compound system of nomenclature described on pp.

[105] L. Larsson, B. Holmstedt, and E. Tjus, *Acta Chem Scand*, **8**, 1563 (1954).

[106] For example, see V. Meyer and P. Jacobson, *Lehrbuch der Organischen Chemie*, 2nd ed., Vol. I, Part I, Verlag Veit u. Cie, Leipzig, Germany, 1907, p. 429, footnote.

90–91 can be applied to the oxyacids of phosphorus based on one phosphorus atom. Examples of this system are $RHPO_2^-$, the alkylhydrodioxyphosphate anion; $R_2PO(OR)$, alkyl dialkyldioxyphosphate; HPO_3^{2-} the hydrotrioxyphosphate anion; and $OP(OR)_3$, trialkyl tetroxyphosphate. The major advantage of this nomenclature is its adaptability to complicated structures involving more than one phosphorus.

Heteropoly Acids and Complex Ions

The phosphomolybdates, -tungstates, and -vanadates are well-known heteropoly acids based on phosphoric acid. These heteropoly acids are discussed in considerable detail on pages 559–569. Hypophosphorous and phosphorous acids also form a number of complicated compounds with the acids of molybdenum, tungsten, and chromium.[107] Although these compounds based on the hypophosphite and phosphite groups have been considered as heteropoly acids, they are not in the same class as the usual heteropoly acids based on phosphoric acid in which there are 9 or 12 atoms of molybdenum, tungsten, or vanadium per atom of phosphorus (see Chapt. 9). Instead, a number of compounds have been made in which there are 6 molybdenum or tungsten atoms per phosphorus atom present as hypophosphite or phosphite Since the usual 6-polyacid involves a six-fold coordination of the central atom, which must be one that can readily exhibit d^2sp^3-hybridization, it is apparent that the 6-polyacids based on phosphite and hypophosphite belong in a different classification. An x-ray investigation of the structure of the heteropoly acids based on the lower oxyacids of phosphorus would be very desirable. It should be noted that in the compounds of molybdenum, tungsten, or chromium with the hypophosphite or phosphite groups, the ratio of transition metal to phosphorus is often lower than six, so that these structures might more logically be classed as salts of relatively simple complex anions, rather than the usual heteropoly acid in which a central atom, such as phosphorus, is surrounded by a complicated three-dimensional network of interconnected oxygen octahedra based on, say, molybdenum.

A number of complex substances involving ferric iron and the hypophos-

[107] A. Rosenheim, M. Schapiro, and A. Italiener, *Z anorg. u. allgem. Chem.*, **129**, 196 (1923) (molybdenum); A. Rosenheim, W. Weinberg, and J. Pinsker, *ibid.*, **84**, 217 (1914) (molybdenum); F. Mawrow and M. Nikolow, *ibid.*, **93**, 170 (1915) (molybdenum); O. W. Gibbs, *Proc. Am. Acad.*, **18**, 235 (1883); *ibid.*, **21**, 97 (1886) (tungsten and molybdenum); A. Rosenheim and A. Wolff, *Z. anorg. u. allgem. Chem.*, **193**, 64 (1930) (tungsten); A. Rogers, *J. Am. Chem. Soc.*, **25**, 298 (1903) (vanadium and tungsten); S. Frommer, *Z. anorg. u. allgem. Chem* , **153**, 134 (1926) (chromium).

phites or phosphites have also been described.[108] In addition, similar compounds based on cobalt and nickel have been investigated to some extent.[109] It has been suggested that the complexes of ferric iron with hypophosphorous acid may be either cationic or anionic; but, except for a single recent investigation,[110] the problem of the structure of these complexes has not been attacked through the use of modern physical methods. Presumably, in these complexes the iron plays the role of a central atom which is coordinated by otherwise isolated phosphorus-containing tetrahedra through sharing of oxygen atoms between the phosphorus and iron atoms. This type of structure may also play a role in the complexes with molybdenum, tungsten, and chromium, so that these atoms might be the central atom instead of the phosphorus. Considerable additional work is needed on the complex salts involving the lower oxyacids of phosphorus before their structures will be known.

ACIDS, SALTS, AND ESTERS BASED ON MORE THAN ONE PHOSPHORUS ATOM

General Theory

As described in Chapters 8, 10, 11, and 12, there are homologous series of condensed phosphoric acids in which the basic PO_4 group of the orthophosphate ion is connected to neighboring PO_4 groups by sharing of oxygen atoms, with only one oxygen being shared between a given pair of groups. Two homologous series in the system of condensed phosphates have been well characterized. One is the series of chain compounds, the polyphosphates, which range from the monomer up to members containing approximately 10^6 phosphorus atoms. The other well-known series consists of ring compounds, the metaphosphates. Rings containing from three to seven phosphorus atoms have been individually characterized, and it is believed that larger rings having at least 15 phosphorus atoms exist in mixtures (see Chapters 11 and 12).

It is possible to share oxygen atoms between the hydrogen-oxygen tetrahedra making up the hypophosphite and phosphite ions, and, of course, there may be structures in which these hydrogen-oxygen tetrahedra share

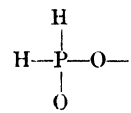
[108] A. Rosenheim, S. Frommer, and W. Händler, *Z. anorg. u. allgem. Chem.*, **153**, 135 (1926); R. F. Weinland and W. Hieber, *ibid.*, **106**, 15 (1919); *Ber.*, **52**, 731 (1919); W Heiber, *Über Komplexverbindungen des dreiwertigen Eisens mit unterphosphoriger Säure*, Thesis, Univ. of Stuttgart, 1919; W. Weinberg, *Über Komplexsäuren der phosphorigen, unterphosphorigen Säure und der Alkylphosphinsäure*, Thesis, Univ. of Berlin, 1913.

[109] A. Rosenheim, S. Frommer, and W. Händler, *Z. anorg. Chem.*, **153**, 135 (1926); S. Frommer and W. Händler, *ibid.*, **153**, 138 (1926).

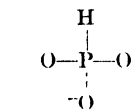
[110] S. Banerjee, *Science and Culture*, **16**, 115 (1950).

oxygen atoms with PO_4 tetrahedra, such as appear in the phosphates. In other words, the building units for making complicated oxyacids held together by P—O—P linkages and containing more than one phosphorus atom per anion are the ones shown below.

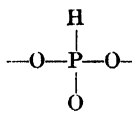
Although each building unit in series 7-37 is shown as a phosphorus atom surrounded by four other atoms (hydrogen or oxygen), it is obvious that these are not the stoichiometrically correct units for building up acids in which single oxygen atoms are shared between pairs of adjacent phosphorus atoms The true stoichiometric formula of each building unit is given in condensed form immediately behind the name of the respective building unit. Thus, if two phosphite end units are put together to make the pyrophosphite anion, the empirical formula of the anion is $2(HPO_{2.5}^{-}) = (H_2P_2O_5)^{2-}$.



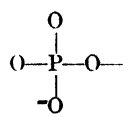
(A) "hypophosphite unit," $H_2PO_{1.5}$



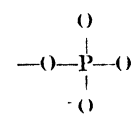
(B) "phosphite end unit," $HPO_{2.5}^{-}$



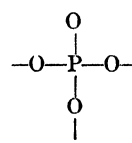
(C) "phosphite middle unit," HPO_2



(D) "phosphate end unit," $PO_{3.5}^{2-}$



(E) "phosphate middle unit," PO_3^{-}



(F) "phosphate branching unit," $PO_{2.5}$

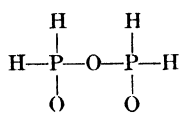
(7-37)

It is obvious that organophosphorus derivatives can be made by substituting organic radicals for the hydrogen atoms of building units A, B, and C.

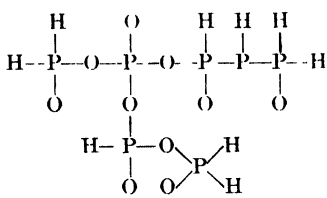
Any acid, salt, or ester of an acid based on more than one phosphorus atom and held together by P—O—P linkages must contain in its structure building units B or D or E, since these are the only units which are ionized or with which ester linkages can be made. In addition to the acids based wholly on P—O—P linkages—which might well be called anhydro acids—it is possible to link the phosphorus atoms directly together, as is the case for the hypophosphate anion, $[O_3PPO_3]^{4-}$. This means that a large variety of lower oxyacids of phosphorus can be produced by putting together structures based on units A–F of series 7-37 and then removing oxygen atoms from various P—O—P linkages in the structure so as to replace these linkages by P—P bonds. Another procedure for obtaining more structures is to exchange a hydrogen on one building unit for an oxygen on a neighboring unit. In this manner, the phosphorus atom from which the hydrogen was taken is made an electron donor to the phosphorus atom which received it. Obviously, there is an extremely large number of possible homologous series obtainable by putting together the six building units

according to various patterns, then removing oxygen atoms from P—O—P linkages according to various other patterns, and exchanging some hydrogens with oxygens. The remainder of this chapter will be primarily devoted to the relatively simple compounds made from building blocks A–F, with P—O—P linkages converted to P—P bonds in some cases. The structures made from only building units D, E, and F, with all P—O—P linkages remaining, are not covered here but are discussed in Chapters 8, 10, 11, and 12.

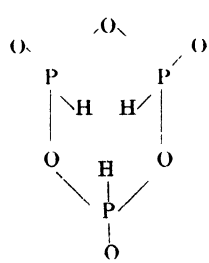
In the case of the condensed phosphates (which are made up of building units D, E, and F) all un-ionized structures must be put together exclusively from building unit F. In other words, the only un-ionized members of the phosphate series are the various varieties of phosphorus pentoxide. However, hydrogen-containing "anhydrides" based on P—O—P linkages can be made by combining structure units A, C, and F and perhaps removing oxygen atoms from some P—O—P linkages. It is also possible to remove up to one oxygen atom per phosphorus (only oxygen atoms not connecting phosphorus atoms being considered) so as to leave an unshared pair of electrons on the phosphorus so treated. Examples of the hypothetical un-ionized compounds obtained by these procedures are given below:



(1) from two hypophosphite units



(2) from three hypophosphite, three phosphite middles, and one phosphate branching unit, with two oxygens removed from P—O—P linkages and one other oxygen removed



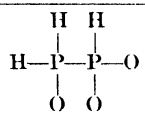
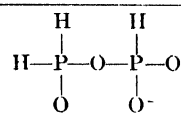
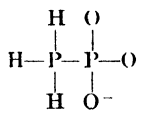
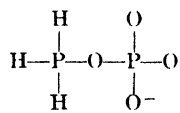
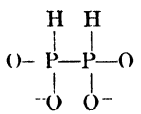
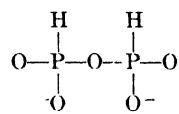
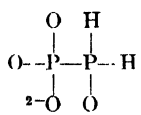
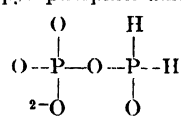
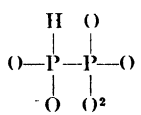
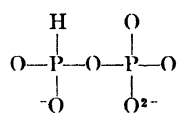
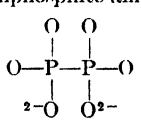
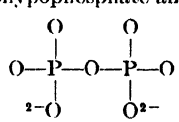
(3) from three phosphite middle units (7-38)

None of these un-ionized structures, with the possible exception of No. 3 which is a "metaphosphorous acid,"[111] is described in the literature. However, it is logical to think that these compounds can exist and will one day be identified.

Oxyacids Based on Two Phosphorus Atoms

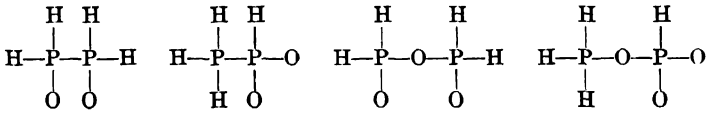
As shown in Table 7-5, there are 12 possible anions in which two phosphorus atoms can each be tetrahedrally surrounded by hydrogen, and/or

TABLE 7-5
Formulas for Anions of the Oxyacids Based on Two Phosphorus Atoms (Peroxyacids Excluded)

 unknown anion	 unknown anion
 unknown anion	 unknown anion
 unknown anion	 pyrophosphite anion
 unknown anion	 unknown anion
 diphosphite anion	 isohypophosphate anion
 hypophosphate anion	 pyrophosphate anion

[111] H. J. van de Stadt, *Z. physik. Chem.*, **12**, 322 (1893).

oxygen, and/or phosphorus atoms, with three- and four-membered rings of atoms being disallowed because of strain. In addition to these 12 anionic structures, there are also four un-ionized "acid-anhydride" structures as shown below.



(7-39)

Five of the 12 anions depicted in Table 7-5 have been isolated and characterized. Three of these five have been known for many years. There is the pyrophosphate anion discovered by Clark in 1828; the hypophosphate anion, discovered by Salzer in 1877; and the pyrophosphite anion, discovered by Amat in 1888. The two remaining ones, the diphosphite and isohypophosphate anions, have been described quite recently by Blaser. All five of these acids are discussed individually below.

It should be noted that the acyl phosphites, described earlier,[73] are closely related in structure to the acids based on two central atoms discussed in this section. However, in the acyl phosphites, RC(O)OPH(O)(OH), one of the central atoms is carbon and the other phosphorus, rather than both being phosphorus.

Pyrophosphites

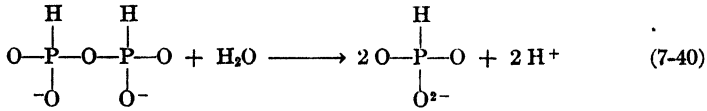
By heating[112] sodium acid orthophosphite, $NaH(O_3PH)\cdot 2.5\ H_2O$, in a vacuum at temperatures around 150°C., until the 2.5 moles of hydrate water and $^1/_2$ mole of water of composition is lost, disodium pyrophosphite, $Na_2(O_2HPOPHO_2)$, is formed. This salt has a reasonably high solubility in water (ca. 40 g./100 g. soln. at 25°C.) and has a natural pH of 7.0. Diammonium, dipotassium, dithallium, calcium, strontium, barium, and lead pyrophosphites have been prepared in a similar manner from the respective acid orthophosphites.[113] Amat made pyrophosphorous acid by reacting the barium pyrophosphite with a stoichiometric amount of sulfuric acid at 0°C. Pyrophosphorous acid in crystalline form (m.p. = +38°C.) is claimed[114] to have also been made by violent agitation of a mixture of phosphorous acid and phosphorus trichloride with a current of carbon dioxide at temperatures near 35°C.

[113] L. Amat, *Compt. rend.*, **106**, 1351, 1400 (1888).

[113] S. J. Kiehl and M. F. Moose, *J. Am. Chem. Soc.*, **60**, 47 (1938); L. Amat, *Ann. chim. et phys.*, **304**, 289 (1891); *Compt. rend.*, **110**, 901 (1890).

[114] V. Auger, *Compt. rend.*, **136**, 814 (1903).

The pyrophosphites undergo hydrolysis[115] to the orthophosphites as shown by the following equation.



(7-40)

The rate of hydrolysis is slowest in neutral solution, being greatly accelerated by either strong acid or strong base. The activation energy is roughly estimated from Amat's data to be 45 kcal./mole. The approximate half lives for hydrolysis at 30°C. are 1000 hr. at pH 5–7, 60 hr. at pH 4, 8 hr. at pH 3, and 5 min. at pH 1.5.

The structure of the inorganic pyrophosphites is reasonably well proven by the method of their preparation, their empirical formula (*e.g.*, $Na_2H_2P_2O_5$), and the fact that they undergo hydrolysis to give orthophosphite. Furthermore, the nuclear magnetic resonance spectrum[26] of the sodium salt exhibits only one spin-spin doublet which proves that the structure is symmetrical, assuming that it contains two phosphorus atoms. This means that the structure given on the left-hand side of equation 7-40 is the correct one for the pyrophosphite ion.

The tetraethyl, tetrapropyl, and tetrabutyl esters of pyrophosphorous acid have been made[116,117] by the following reaction between sodium dialkyl phosphite and the dialkyl chlorophosphite.

$$(RO)_2PONa + ClP(OR)_2 \longrightarrow NaCl \downarrow + (RO)_2POP(OR)_2 \qquad (7\text{-}41)$$

These esters are liquids which can be distilled in a vacuum and which form adducts with two moles of cuprous halides; *e.g.*, tetraethyl pyrophosphite boils at 102–104°C. under pressure of 11 mm. of Hg and has a 2 CuCl adduct that melts at 112°C. Formation of the adducts is a proof that the fully substituted esters are derivatives of triply connected phosphorus.

Pyrophosphonates

Several esters of pyrophosphonic acid, (HO)(O)RPOPR(O)(OH), have been made.[117–119] The ethyl derivative was prepared by reacting ethyl

[115] S. J. Kiehl and M. F. Moose, *J. Am. Chem. Soc.*, **60**, 257 (1938); L. Amat, *Compt. rend.*, **108**, 1056 (1889); *ibid.*, **112**, 527, 614 (1891).

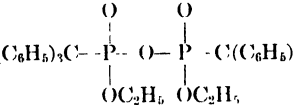
[116] A. E. Arbusov and V. S. Abramov, *Trudy Kazan Khim.-Tekhnol. Inst. im. S. M. Kirova*, **1**, 28 (1935); A. E. Arbusov and B. A. Arbusov, *Zhur. Obshcheĭ Khim.*, **2**, 371 (1932).

[117] A. E. Arbusov and B. A. Arbusov, *J. prakt. Chem.*, **31**, 337 (1931); *Zhur. Obshcheĭ Khim.*, **2**, 348 (1932); A. E. Arbusov and A. I. Razumov, *ibid.*, **7**, 1762 (1937).

[118] H. H. Hatt, *J. Chem. Soc.*, **1933**, 776

[119] A. Michaelis, *Ann.*, **315**, 43 (1901).

iodide with tetraethyl hypophosphate, $(C_2H_5O)_2OPPO(OC_2H_5)_2$, whereas the dimethyl and diethyl esters of triphenylmethanepyrophosphonate were obtained by heating the respective dialkyl triphenylmethanephosphonate with phosphorus pentachloride As shown by the following formula (7-42), each phosphorus atom in diethyl triphenylmethanepyrophosphonate is asymmetric, although the compound itself is symmetric. This means that the two phosphorus atoms should be optically active. Hatt[118] separated the compound into two forms, m p. 223 and 230°C. It has been suggested[118,120] that one form is the racemate and the other the meso-form, although it is possible that two different anions, other than optical isomers, may be involved [*e.g.*, (RO)(R)(O)POP(O)(R)(OR) and (RO)(R)(O)-PP(O)(OR)$_2$].



(7-42)

Diphosphites

Following up some work started before 1935,[121] Blaser announced[122,123] in 1953, a new acid of phosphorus which is an isomer of pyrophosphorous acid, $H_4P_2O_5$. This new acid, called diphosphorous acid, was isolated from hydrolysates of phosphorus tribromide or triiodide.[124] The normal sodium salt of this acid has the formula, $Na_3HP_2O_5$, and has been obtained in the anhydrous form by heating the hexahydrate at 100°C. It has also been crystallized from water as a dodecahydrate at 0°C and a hexahydrate at 30°C. The trisodium salt is a stable compound, both as the hexahydrate and in neutral aqueous solution. The diphosphite anion is oxidized quickly and quantitatively with iodine in sodium bicarbonate solution to give the hypophosphate ion, whereas the pyrophosphite anion is resistant to oxidation by iodine under the same conditions. Likewise, bromine in acid also oxidizes diphosphorous acid to hypophosphoric acid. On the other hand, bromine in sodium bicarbonate solution gives essentially a 100% yield of

[120] F. G. Mann, *J. Chem Soc*, **1945**, 65.

[121] B. Blaser, *Ber.*, **68B**, 1670 (1935).

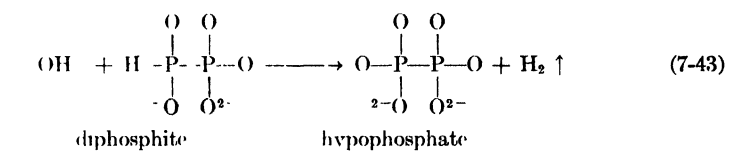
[122] B. Blaser, *Chem. Ber.*, **86**, 563 (1953).

[123] B. Blaser, *I. New Acids of Phosphorus with Low Oxidation Value; II. Interanhydrization of Acids of Phosphorus in Aqueous Solution*, Henkel Co., Duesseldorf, Germany, May, 1956. This manuscript covers talks given at the 129th Meeting of the American Chemical Society at Dallas, Texas, April 9–10, 1956, and at a University of Chicago seminar April 23, 1956

[124] E Thilo and D. Heinz, *Z. anorg. u. allgem. Chem*, **281**, 303 (1955)

the pyrophosphate anion from the oxidation of the diphosphite anion. The hypophosphate anion under the same conditions is also oxidized to pyrophosphate.

Unlike the pyrophosphite anion which is readily split by hydrolysis in alkaline solution, the diphosphite anion is quite stable in hot alkaline solution. Thus, boiling for 60 min. in 2 *N* sodium hydroxide gave no change. On the other hand, heating the trisodium diphosphite in highly concentrated sodium hydroxide at 160°C. for several hours leads to the formation of tetrasodium hypophosphate with evolution of hydrogen. All of these reactions have been interpreted by Blaser to mean that the diphosphite anion has the following structure, $^{-}O_2(H)PPO_3^{2-}$. The reaction with highly concentrated sodium hydroxide is given in equation 7-43 below, which is very similar to the reaction of the hypophosphite ion shown in equation 7-8.



(7-43)

Indeed, it appears that there may be a general reaction between concentrated alkali and a hydrogen atom attached directly to a phosphorus connected to two (hydrogen or phosphorus) atoms, in an anionic structure.

Blaser's structure for the diphosphite ion has been substantiated by nuclear magnetic resonance measurements[125] from which a typical spectrum is shown in Figure 7-5. Because of close spin-spin coupling between the hydrogen and the two phosphorus atoms directly connected to each other, the nuclear magnetic resonance spectrum is not simply understood but must be interpreted quantum mechanically in terms of three coupled nuclei of spin $^1/_2$. The Zeeman levels shown in Figure 7-5 were calculated from the following Hamiltonian,[126] representing the total energy of the system on the assumption that the spin-spin coupling of the hydrogen and either phosphorus is small compared to the difference between the resonance frequencies of the hydrogen and either phosphorus.

$$H = -h\{\omega_H I_H^0 + \omega_{P1} I_{P1}^0 + \omega_{P2} I_{P2}^0 + J_{HP1} I_H^0 I_{P1}^0 + J_{HP2} I_H^0 I_{P2}^0 + J_{P1P2}[I_{P1}^0 I_{P2}^0 + {}^1/_2(I_{P1}^+ I_{P2}^- + I_{P1}^- I_{P2}^+)]\} \quad (7\text{-}44)$$

[125] C. F. Callis, J R Van Wazer, J. N Shoolery, and W. C. Anderson, *J. Am. Chem Soc.*, **79**, 2719 (1957).

[126] W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

where H is the Hamiltonian operator; h is the quantum of action divided by 2π; ω is the resonance frequency; I^0 is the z-component of the spin operator chosen in the direction of the applied magnetic field; J is the spin-coupling constant; $I^{\pm}$ is the complex spin-operator in the plane perpendicular to the field; and the subscripts H, $P1$, and $P2$ refer to the hydrogen

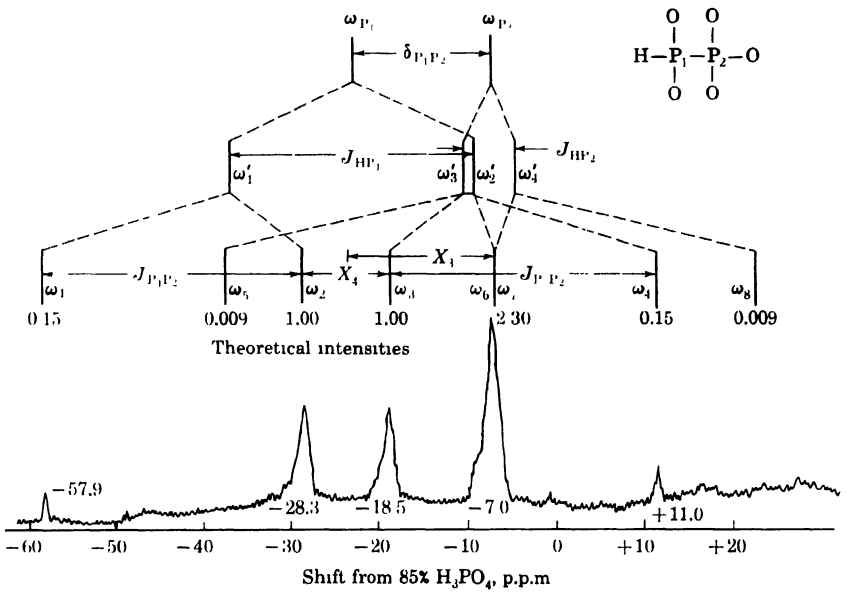


Fig 7-5. Zeeman levels and observed phosphorus spectrum for the "diphosphite" anion at a field of 9440 gauss. Because of saturation effects at the high rf field used to show up the small peaks, the peak areas are not strictly proportional to their predicted values. The measured values of X_3 and X_4 are 16.4 and 9.8 p.p.m., respectively. At the 7140 gauss field, the observed values of X_3 and X_4 are 21.9 and 9.5 p.p.m. compared to the calculated values of 21.6 and 10 p.p.m., respectively.

nucleus, the phosphorus adjacent to the hydrogen, and the other phosphorus nucleus, respectively. The resonance frequencies of the phosphorus nuclei derived from a solution of equation 7-44 are

$$\omega_1 = \omega_{P2} + {}^1/_2\delta + {}^1/_2(J' + J_{P1P2}) + {}^1/_2\sqrt{(\delta + J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}45)$$

$$\omega_2 = \omega_{P2} + {}^1/_2\delta + {}^1/_2(J' - J_{P1P2}) + {}^1/_2\sqrt{(\delta + J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}46)$$

$$\omega_5 = \omega_{P2} + {}^1/_2\delta + {}^1/_2(J' - J_{P1P2}) + {}^1/_2\sqrt{(\delta - J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}47)$$

$$\omega_6 = \omega_{P2} + {}^1/_2\delta - {}^1/_2(J' + J_{P1P2}) + {}^1/_2\sqrt{(\delta - J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}48)$$

$$\omega_3 = \omega_{P2} + {}^1/_2\delta + {}^1/_2(J' + J_{P1P2}) - {}^1/_2\sqrt{(\delta + J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}49)$$

$$\omega_4 = \omega_{P2} + {}^1/_2\delta + {}^1/_2(J' - J_{P1P2}) - {}^1/_2\sqrt{(\delta + J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}50)$$

$$\omega_7 = \omega_{P2} + {}^1/_2\delta - {}^1/_2(J' - J_{P1P2}) - {}^1/_2\sqrt{(\delta - J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}51)$$

$$\omega_8 = \omega_{P2} + {}^1/_2\delta - {}^1/_2(J' + J_{P1P2}) - {}^1/_2\sqrt{(\delta - J'')^2 + J_{P1P2}{}^2} \quad (7\text{-}52)$$

where δ is the chemical shift between the phosphorus nuclei, and

$$J' = {}^1/_2(J_{HP1} + J_{HP2}) \quad (7\text{-}53)$$

$$J'' = {}^1/_2(J_{HP1} - J_{HP2}) \quad (7\text{-}54)$$

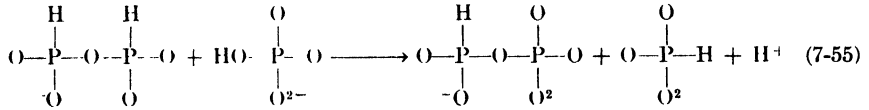
In addition to measuring the phosphorus nuclear magnetic resonance spectrum shown in Figure 7-5 at an applied field of 9440 gauss, the phosphorus spectrum was remeasured at 7150 gauss; and the hydrogen resonance spectrum was also measured on a solution of trisodium diphosphite in D_2O. The hydrogen spectrum gave directly the phosphorus-hydrogen spin-coupling constants, J_{HP1} and J_{HP2}. Since four lines were observed in the hydrogen spectrum, it is obvious that the hydrogen atom is strongly coupled to both of the phosphorus nuclei.

Interpretation of measurements of the phosphorus and hydrogen spectra in terms of equations 7-45–7-52 gave spin-spin coupling constants of 480 cycles/sec. for the P-P coupling (J_{P1P2}), 444 cycles/sec. for the coupling between hydrogen and the nearest phosphorus (J_{HP1}), and 94 cycles/sec. for the coupling between the hydrogen and the phosphorus once removed (J_{HP2}). In addition, the chemical shift, δ, between the two phosphorus nuclei was found to be 15.6 p.p.m. of the applied magnetic field. These values are all of the magnitude to be expected from the structure of the anion postulated by Blaser and, when combined with the chemical reactions discussed above, give a rather convincing proof for the structure.

Isohypophosphates

In addition to the diphosphite, Blaser has recently investigated another new anion based on two phosphorus atoms.[123] The acid of this new anion has the formula, $H_4P_2O_6$, which makes it isomeric with hypophosphoric acid, so that it has been named isohypophosphoric acid. This new acid is prepared in yields up to about 25% of theory by heating mixtures of phosphorous acid and orthophosphoric acid in a vacuum. Similar results are obtained when phosphorous acid is mixed with phosphorus pentoxide or

the strong condensed phosphoric acids. The isohypophosphate anion can also be made by a type of reorganization process (which Blaser calls "interanhydrization") between pyrophosphorous acid and orthophosphoric acid in the absence of water or between the pyrophosphite and orthophosphate ions in neutral solution, as shown below:



(7-55)

In addition, it can be prepared in small yields by dropping phosphorus oxychloride into an aqueous phosphite solution, kept approximately neutral by addition of sodium bicarbonate. Isohypophosphoric acid was first postulated by Nylén as forming from the decomposition of hypophosphoric acid;[127] and, indeed, Blaser has isolated the sodium salt of isohypophosphoric acid from the complex mixture of anhydrous acids of phosphorus obtained from the spontaneous decomposition of hypophosphoric acid.

The isohypophosphate anion is separated from the mixtures in which it is formed by first oxidizing whatever phosphite is present to orthophosphate through use of iodine in neutral aqueous solution. The trisodium isohypophosphate can be obtained in analytically pure form by repeated precipitation with alcohol from the resulting isohypophosphate-orthophosphate solution, followed by precipitation of the last portion of orthophosphate as the lead salt. Trisodium isohypophosphate, $Na_3HP_2O_6$, has been obtained as well-crystallized octa- and tetrahydrates but not as the anhydrous salt.

Isohypophosphoric acid is found to be tribasic, and the trisodium salt is allegedly stable in solid form and in neutral aqueous solution. In acid and alkaline solutions, the isohypophosphate anion hydrolyzes to an equimolar mixture of the phosphite and orthophosphate anions. Thus, in 0.2 *N* HCl at 25°C., the half life is about 3 min., and in 1 *N* NaOH at 20°C. the half life is 7 3 hr. In stability to hydrolysis, the isohypophosphate anion lies between the pyrophosphite and pyrophosphate anions.[123] With respect to solubility of its salts with myltiply charged or heavy metal ions, the isohypophosphate anion also lies between these two other anions. Thus, the solubility of barium isohypophosphate is approximately 1 g./l. as compared to the very insoluble barium pyrophosphate and the reasonably soluble barium pyrophosphite.

The nuclear magnetic resonance spectrum[125] of the isohypophosphate anion obtained on a concentrated aqueous solution of trisodium isohypo-

[127] P. Nylén, *Z anorg. u allgem Chem.*, **229**, 36 (1936).

phosphate is shown in Figure 7-6. This spectrum can be simply interpreted, without special reference to quantum mechanics, since we can make the *a priori* assumption that $J_{HP1} >> J_{HP2}$ and $J_{HP1} >> J_{P1P2}$ for this ion. This means that the complicating cross-terms in equations 7-44–7-54 become inappreciably small. Thus, peaks 1*A* and 1*B* in Figure 7-6 are due to the phosphorus atom to which the hydrogen is directly connected. The large spin-spin coupling between the hydrogen and this phosphorus is reflected in the considerable distance of separation between these peaks. Peak 2 in Figure 7-6 corresponds to the phosphorus atom to which no hydrogen is connected. The area of peak 2 is approximately equal to the sum of the areas of peaks 1*A* and 1*B*. Furthermore, the splitting of all three peaks

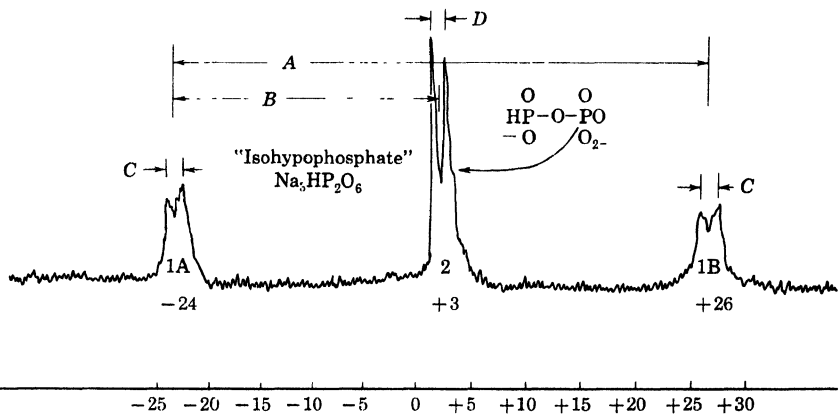
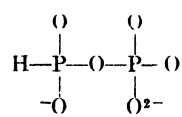


Fig 7-6. Nuclear magnetic resonance spectrum of the "isohypophosphate" anion at 7140 gauss and 12.3 megacycles. A = 50 p p m or 0.36 gauss; B = 27 p.p.m or 0.19 gauss; C = 0.01 gauss; D = 0 01 gauss.

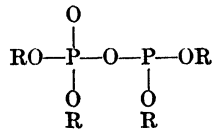
into doublets is attributable to the spin-spin coupling of the two phosphorus atoms, as attenuated by the bridging oxygen. This spectrum offers a simple, direct proof that the isohypophosphate anion has the following structure.



(7-56)

When halogens are reacted with dialkyl sodium phosphites, a number of different organic compounds are obtained, including tetraalkyl pyrophos-

phites, hypophosphates, and pyrophosphates. Tetraethyl and tetrapropyl "hypophosphates," prepared by this method have been described by Arbusov and coworkers.[117] It is quite possible that these compounds are esters of isohypophosphoric acid instead of being esters of hypophosphoric acid The general formula for the tetraester of isohypophosphoric acid is



(7-57)

Preparation and Structure of Hypophosphoric Acid, Its Salts and Esters[128]

As was noted previously, Salzer[3] discovered hypophosphoric acid in the mixture of oxyacids of phosphorus obtained by the slow oxidation of elemental phosphorus in the presence of water. Although this method is still used occasionally for the preparation of hypophosphoric acid,[129] the oxidation of elemental phosphorus by aqueous solutions of oxidizing agents is now usually employed in making hypophosphates. Probably the most reliable preparation which can be recommended is based on the oxidation of red phosphorus by sodium chlorite.[130] In this procedure, a solution of technical-grade sodium chlorite is slowly drawn through a cooled reaction chamber containing powdered red phosphorus mixed with glass beads. After addition of charcoal for decolorization, the solution of the reaction products is allowed to stand overnight. It is then filtered and brought to pH 5.4 by addition of sodium hydroxide. After heating, the solution is cooled to promote crystallization. There is a yield of about 40% $Na_2H_2P_2O_6 \cdot 6\ H_2O$, based on the $NaClO_2$ used. Another good procedure for the preparation of hypophosphates is the oxidation of yellow phosphorus by copper nitrate. Detailed directions for carrying out this preparation are to be found in the literature.[131,132] Oxidation of elemental phosphorus to form hypophosphates has also been carried out by hypochlorite,[133] alkaline

[128] T. Milobedzki, *Roczniki Chem.*, **24**, 48 (1950) gives a review based on a somewhat different viewpoint than that employed herein.

[129] J. Cavalier and E. Cornec, *Bull. soc. chim. France*, **5**, 1058 (1910).

[130] E. Leininger and T. Chulski, *Inorganic Synthesis*, ed. J. C. Bailar, McGraw-Hill Book Co., New York, 1953, Vol. IV, p. 68; *J. Am. Chem. Soc.*, **71**, 2385 (1949).

[131] W. Jung, *Anales soc. quím. argentina*, **30**, 99 (1942); *ibid.*, **32**, 105 (1944); F. Tauchert, *Z. anorg. Chem.*, **79**, 350 (1913).

[132] A. Rosenheim and J. Pinsker, *Ber.*, **43**, 2003 (1910).

[133] M. Speter, *Rec. trav. chim.*, **46**, 588 (1927); J. Probst, *Z. anorg. u. allgem. Chem.*, **179**, 155 (1929).

permanganate,[134] hydrogen peroxide,[134] or iodine.[135] In addition, relatively good yields of hypophosphoric acid have been obtained by reducing[136] phosphoric acid and by oxidizing the products of hydrolysis of P_2I_4 or PI_3 with iodine.[137]

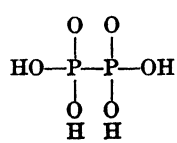
The soluble salts of hypophosphoric acid are usually prepared by neutralizing the acid or by running the sodium salt through an ion-exchange column to get the acid which is then neutralized. The poorly soluble salts are readily made by precipitating from a solution of sodium hypophosphate or from a solution of hypophosphoric acid. Tetraethyl hypophosphate (or isohypophosphate) has been obtained[138] by the following reaction:

$$(C_2H_5O)_2(O)PCl + [Na(O)P(OC_2H_5)_2 \text{ or } (NaO)P(OC_2H_5)_2] \longrightarrow$$
$$[(C_2H_5O)_2(O)PP(O)(OC_2H_5)_2 \text{ or } (C_2H_5O)_2POP(O)(OC_2H_5)_2] + NaCl \downarrow \quad (7\text{-}58)$$

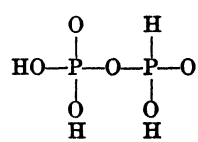
Another interesting reaction[139] for the preparation of hypophosphate (or perhaps isohypophosphate) esters is the following:

$$2\,[(RO)_2P(O)Na \text{ or } (RO)_2P(ONa)] + 2\,(C_6H_5)_3CBr \longrightarrow$$
$$2\,(C_6H_5)_3C + [(RO)_2(O)PP(O)(OR)_2 \text{ or } (RO)_2POP(O)(OR)_2] + 2\,NaBr \quad (7\text{-}59)$$

Ever since its discovery nearly a century ago, the structure of hypophosphoric acid has been the subject of considerable study and conjecture. It is instructive to review the various ideas suggested for the structure of this acid. Salzer[3] concluded that the acid was present as a dimer of the empirical formula, H_2PO_3, *i.e.*, the acid was $H_4P_2O_6$. He came to this conclusion largely because he was able to make four different salts of monovalent cations, viz., $NaH_3P_2O_6$, $Na_2H_2P_2O_6$, $Na_3HP_2O_6$, and $Na_4P_2O_6$. He then went on to conjecture as to what was the structure of this acid and concluded that it was possibly either I or IV of the structures given below:



(I)



(II)

[134] F. Vogel, *Z. angew. Chem.*, **42**, 263 (1929).

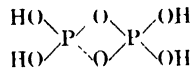
[135] T. Milobedzki, J. H. Kolitowska, and Z. Berkan, *Roczniki Chem.*, **17**, 620 (1937).

[136] J. H. Kolitowska, *Z. anorg. u. allgem. Chem.*, **230**, 310 (1937).

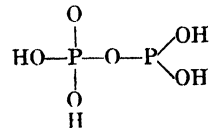
[137] J. H. Kolitowska, *Roczniki Chem.*, **17**, 616 (1937).

[138] T. Milobedzki and J. Walczynska, *Roczniki Chem.*, **8**, 486 (1928).

[139] A. E. Arbusov, *Trudy Sessii Akad. Nauk Org. Khim.*, **1939**, 211; A. E. Arbusov and B. A. Arbusov, *Ber.*, **62**, 1871 (1929); *J. Russ. Phys.-Chem. Soc.*, **61**, 1923 (1929).



(III)



(IV) (7-60)

In spite of the fact that Salzer succeeded in making the salt, $K_3H_5(P_2O_5)_2 \cdot 2\,H_2O$, and similar intermediate salts, Bansa,[140] who was the next man to concern himself with the question of structure, accepted the double formula of Salzer and supported the symmetrical formula, I, on the basis that isomeric dipotassium disodium hypophosphates were not obtained. Obviously, this was before acceptance of the concept of ionization which makes the idea of such isomerization due to mixed cations meaningless.

In 1906 Parravano and Marini[141] came to the conclusion that the formula of hypophosphoric acid was $H_4P_2O_6$, based on interpretation of conductivity and transport-number measurements on aqueous solutions of the acid and two of its sodium salts. Some of the evidence of these authors was based on comparison with pyrophosphoric acid, which they correctly assumed to have the formula, $H_4P_2O_7$. In the same year, Rosenheim *et al.*[142] came to the opposite conclusion, that the acid possessed the simple formula H_2PO_3. They based the monomeric formulation on the determination of boiling-point elevations of solutions of methyl hypophosphate (?) in ethyl bromide, ethyl iodide, and chloroform. For comparison, they showed that ethyl pyrophosphate had a molecular weight corresponding to the formula, $(C_2H_5O)_4P_2O_3$. In 1909, Rosenheim[143] confirmed his original view by additional cryoscopic measurements on alleged esters of hypophosphoric acid. However, in the same year Cornec[144] supported the double formula with his interpretation of measurements on freezing-point depression of aqueous solutions of sodium, potassium, and ammonium hypophosphates. Rosenheim said that this was merely association in aqueous solution.

In a study of hydrolysis of hypophosphoric acid, Van Name and Huff[145] concluded in 1918 that the reaction exhibited a first-order rate and, there-

[140] C. Bansa, *Z. anorg. Chem.*, **6**, 128, 143 (1894).

[141] N. Parravano and C. Marini, *Atti. accad. nazl Lincei, Rend Classe sci. fis mat. e nat.*, **15**, 203, 305 (1906).

[142] A. Rosenheim, W. Stadler, and F. Jacobsohn, *Ber.*, **39**, 2837 (1906).

[143] A. Rosenheim and J. Pinsker, *Z. anorg. Chem.*, **64**, 327 (1909); A. Rosenheim and M. Pritze, *Ber.*, **41**, 2708 (1908).

[144] E. Cornec, *Bull. soc. chim*, **5**, 1081, 1121 (1909); *Compt. rend.*, **150**, 108 (1910).

[145] R. G. Van Name and W. J. Huff, *Am. J. Sci*, **45**, 91, 103 (1918).

fore, that the anion in solution must be $P_2O_6^{4-}$; since, if it were PO_3^{2-}, two molecules would be required in the hydrolysis to produce phosphorous and phosphoric acids in equimolar quantities and, consequently, according to the rate theory of that period, a second-order constant should have been found. This work was repeated ten years later by Rosenheim and Zilg,[146] who were finally convinced that, at least in dilute acid solution, the formula must be double, *i.e.*, $(O_3P. .PO_3)$. The existence of the double formula was settled beyond any reasonable doubt by Bell and Sugden[147] in 1933. They argued that, since H_2PO_3 and its ions contain an odd number of extranuclear electrons and $H_4P_2O_6$ and its ions do not, the hypophosphates should be paramagnetic if they exhibit the simpler structure. Experimentally it was found that a number of hypophosphate salts, as well as some alleged esters of hypophosphoric acid, were all diamagnetic and must, therefore, be derived from an acid which was a polymer (not necessarily the dimer) of the simple empirical formula

It is interesting to note that a study[148] was carried out in 1937 on the lowering by hypophosphates of the freezing point of eutectic mixtures (in which electrolytes give a mole lowering proportional to the number of ions other than the ions in common with the salt used in the eutectic mixture). This technique, which is acceptable to modern theory, supported the double structure for the hypophosphate ion, viz., $P_2O_6^{4-}$. This double structure is also in accord with Raman spectral data[149] which definitely rule out a monomeric ion, PO_3^{2-}.

Now that the question of molecular size was settled, the next problem was to decide on the structural formula. From measurements of ionization constants, Treadwell and Schwarzenbach[150] concluded that the hypophosphate ion was symmetrical; *i.e.*, it corresponds to either formula I or III shown in series 7-60. Further evidence supporting structure I was then presented by Nylén and Stelling,[151] on the basis of (1) the resistance of the acid and its salts to oxidation and (2) the position and sharpness of the absorption edge in the x-ray absorption of solid hypophosphates. Very shortly after this work was published in 1933, Blaser and Halpern[152] came forward with a paper strongly supporting the unsymmetrical structure corresponding to formulas IV or II. In this article, a quantitative study

[146] A. Rosenheim and H. Zilg, *Z. physik. Chem.*, **139A**, 12 (1928).
[147] F. Bell and S. Sugden, *J. Chem. Soc.*, **1933**, 48.
[148] H. J. Muller, *Ann. chim.*, **8**, 143 (1937).
[149] J. Gupta and A. K. Majumdar, *J. Indian Chem. Soc.*, **19**, 286 (1942).
[150] W. D. Treadwell and G. Schwarzenbach, *Helv. Chim. Acta*, **11**, 405 (1928).
[151] P. Nylén and O. Stelling, *Z. anorg. u. allgem Chem.*, **212**, 169 (1933).
[152] B. Blaser and P. Halpern, *Z. anorg. u. allgem. Chem.*, **215**, 33 (1933).

was presented on the oxidation of hypophosphates to pyrophosphates by bromine—a reaction discovered 50 years earlier by Salzer.[3] Since a 97% yield of pyrophosphate was obtained in about 15 min. at pH 7–8, it was concluded that the hypophosphate anion was a dimer of the empirical formula and must contain a P–O–P linkage, according to the most obvious reaction mechanism, depicted below in equation 7-61. This inapplicable equation was the basis for supporting formulas II or IV.

$$^{2-}O_3POP(H)O_2^- + (O) \longrightarrow {}^{2-}O_3POPO_3^{2-} + H^+ \qquad (7\text{-}61)$$

Formula III, having a double oxygen bridge, was ruled out on the basis that such a structure would not hydrolyze smoothly to phosphorous and phosphoric acids. It should also be noted[153] that in formula III each phosphorus atom would have nine electrons in its outer valence shell which would make the salts paramagnetic—although they were shown to be diamagnetic by Bell and Sugden. The paper by Blaser and Halpern was immediately answered by Nylén and Stelling,[154] who reemphasized the value of their studies concerned with the x-ray absorption edge, and by Hantzsch.

X-ray studies, primarily by Raistrick,[153] have shown that the symmetry of the ammonium hypophosphate crystal is in accord with structure I. It should be noted that the structure of ammonium hypophosphate is very similar to that of ammonium bicarbonate, in which the planar carbonate groups are arranged in columns parallel to the *C* axis. This isomorphism is in accord with structure I. Probably the most impressive proof for structure I is found in nuclear magnetic resonance studies in which the hypophosphate ion exhibits only a single resonance peak.[125] This proves that the structure of the molecule-ion, assuming two phosphorus atoms, is symmetrical and that no hydrogens are attached directly to a phosphorus atom.

Properties and Reactions of the Hypophosphates

Hypophosphoric acid has been obtained in an anhydrous form and as a monohydrate, $H_4P_2O_6 \cdot H_2O$, and a dihydrate, $H_4P_2O_6 \cdot 2\,H_2O$. The anhydrous acid melts at 70°C., whereas the mono- and dihydrates melt at 79.5–81.5°C. and 62–62.5°C., respectively. As previously pointed out,[127] both of these crystalline hydrates of hypophosphoric acid slowly undergo spon-

[153] B. Raistrick, *Sci. J. Roy. Coll. Sci.*, **19**, 9 (1949); B. Raistrick and E. Hobbs, *Nature*, **164**, 113 (1949); R. Brooks and T. C. Alcock, *ibid.*, **166**, 435 (1950).

[154] P. Nylén and O. Stelling, *Z. anorg. u. allgem. Chem.*, **218**, 301 (1934); A. Hantzsch, *ibid.*, **221**, 63 (1943).

taneous decomposition at room temperature to give a mixture of the oxyacids of phosphorus, including orthophosphorous acid, orthophosphoric acid, and isohypophosphoric acid.[123] Dilute solutions of pure hypophosphoric acid can be stored for a reasonable length of time and even boiled without change, but decomposition of concentrated solutions takes place

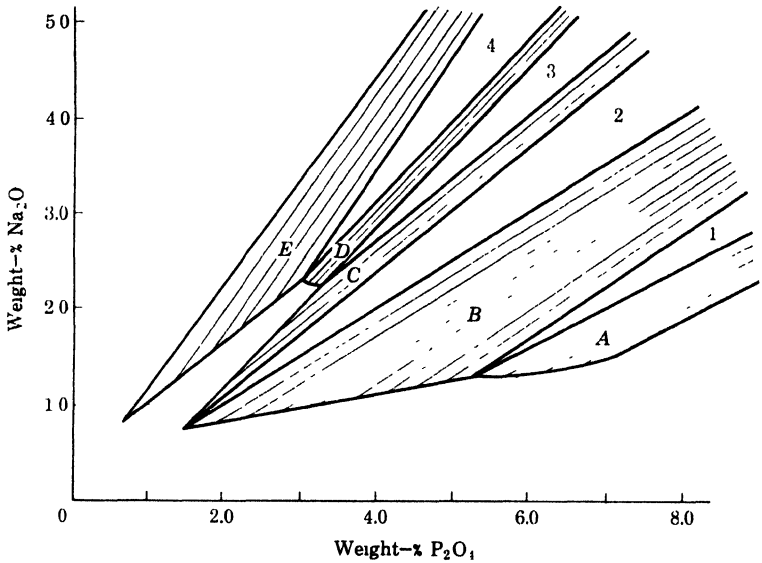


Fig. 7-7. The sodium hypophosphate system, Na_2O–H_2O–P_2O_5, at 30°C. The two-phase areas are lettered: A = $Na_3H_5(P_2O_6)_2$ plus solution; B = $Na_2H_2P_2O_6 \cdot 6H_2O$ plus solution; C = $Na_5H_3(P_2O_6)_2 \cdot 20H_2O$ plus solution; D = $Na_3HP_2O_6 \cdot 9H_2O$ plus solution; E = $Na_4P_2O_6 \cdot 10H_2O$ plus solution. The three-phase areas are numbered

if the temperature much exceeds 30°C. In dilute solution the reaction is one of hydrolysis to form orthophosphorous and orthophosphoric acids (see equation 7-63 below).

The system Na_2O–H_2O–P_2O_5 has been studied at 30°C.,[155] and the results are shown in Figure 7-7, from which it can be seen that there are salts having the following Na_2O/P_2O_5 mole ratios: 2.00, 1.50, 1.25, 1.00, and 0.75. These values correspond to the salts $Na_4P_2O_6 \cdot 10\,H_2O$, $Na_3HP_2O_6 \cdot 9\,H_2O$,

[155] I. Muller, *Über die Basizität der Unterphosphorsaure*, Thesis, Univ. of Leipzig, 1916

$Na_5H_3(P_2O_6)_2 \cdot 20\ H_2O$, $Na_2H_2P_2O_6 \cdot 6\ H_2O$ and $Na_3H_5(P_2O_6)_2$, respectively In Figure 7-7 the weight percentage of H_2O should be obtained by difference. The compositions corresponding to the various solid crystalline phases are not shown The capital letters represent two-phase areas covered

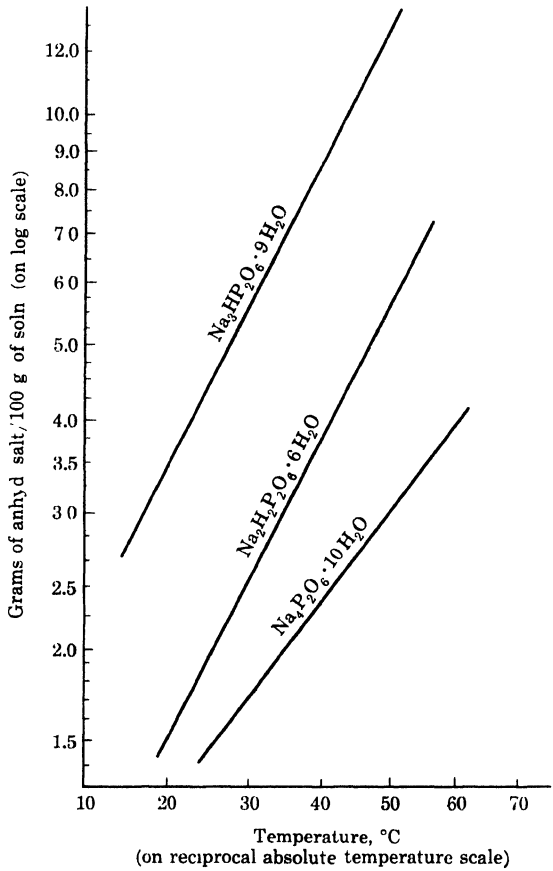


Fig. 7-8. Solubility of some sodium hypophosphates in water as a function of temperature.

by tie lines extending from these solid phases to the heavy line which denotes the composition of the saturated solution. Thus, the region covered by the tie lines corresponds to a mixture of saturated solution and the corresponding pure crystalline phase. In the areas denoted by Arabic numbers there are two crystalline solids in equilibrium with a saturated solution of fixed

composition. The region of homogeneous solution lies on the other side of the heavy line from the areas covered by tie lines.

The temperature variation of solubility of three sodium hypophosphates is shown in Figure 7-8, from which it should be noted that these salts are only moderately soluble with respect to sodium salts in general. The potassium hypophosphates which have been described, mostly by Salzer,[8] are the following: $K_4P_2O_6 \cdot 8\ H_2O$, $K_4P_2O_6 \cdot 2\ H_2O$, $K_4P_2O_6$; $K_3HP_2O_6 \cdot 3\ H_2O$, $K_3HP_2O_6$; $K_2H_2P_2O_6 \cdot 3\ H_2O$ (?), $K_2H_2P_2O_6 \cdot 2\ H_2O$, $K_2H_2P_2O_6$; $K_3H_5(P_2O_6)_2 \cdot 2\ H_2O$, $K_3H_5(P_2O_6)_2$; and $KH_3P_2O_6$.

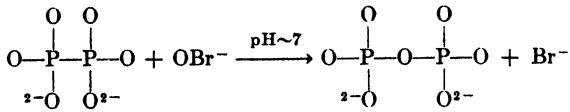
Many of the insoluble hypophosphates formed by precipitation are also hydrated,[20] viz., $Mg_2P_2O_6 \cdot 12\ H_2O$, $Ca_2P_2O_6 \cdot 2\ H_2O$, $Sr_2P_2O_6 \cdot 2\ H_2O$, $Cu_2P_2O_6 \cdot 6\ H_2O$. Some double salts of hypophosphoric acid have also been crystallized. Examples[20] are $Na_2K_2P_2O_6 \cdot 9\ H_2O$, $K_6CuH_8(P_2O_6)_4 \cdot 15\ H_2O$, $K_2CoP_2O_6 \cdot 5\ H_2O$, $K_6CoH_8(P_2O_6)_4 \cdot 15\ H_2O$, $K_2NiP_2O_6 \cdot 6\ H_2O$, and $K_6NiH_8(P_2O_6)_2 \cdot 15\ H_2O$. Acid salts of the alkaline earth metals can be prepared by dissolving the normal salt in hypophosphoric acid and then crystallizing by evaporating under vacuum or by adding alcohol. For calcium, strontium, and barium the acid salt has the formula, $M_2H_2P_2O_6 \cdot 2\ H_2O$. The hypophosphate ion apparently can form some type of complex anion with molybdate, as evidence by the formulas, $Na_4P_2O_6 \cdot 2\ MoO_3$ and $Na_4P_2O_6 \cdot 4\ MoO_3 \cdot 16\ H_2O$.[20]

From pH measurements, the ionization constants of hypophosphoric acid were reported[150] to be K_1 = about 6×10^{-3}, K_2 = about 1.5×10^{-3}, $K_3 = 5.4 \times 10^{-8}$, and $K_4 = 0.93 \times 10^{-10}$ at 25°C. However, colligative data[132] indicate that hypophosphoric acid is ionized to a greater extent than is implied by the e.m.f. measurements on which these constants are based.

As might be expected, there is no exchange of radioactive phosphorus between the hypophosphate, orthophosphate, or pyrophosphate ions.[156] As was noted previously, the hypophosphate anion is quite resistant to oxidation, since neither halogens nor salts of noble metals nor nitric acid[157] exerts the slightest oxidizing action in acid media. Only dichromate and permanganate in acid solution at high temperatures effect oxidation; and this is probably primarily due to hydrolysis to phosphorous and phosphoric acids. The oxidizing action of bromine to convert the hypophosphate anion into the pyrophosphate ion should be excluded from this generality. This reaction with bromine is extremely slow outside the pH range of 5–11, but, as previously noted, occurs[152] quite rapidly in neutral solution, according to equation 7-62:

[156] T. Moeller and G. H. Dawson, *J. Am. Chem. Soc.*, **74**, 6122 (1952).

[157] B. Blaser, *Z. physik. Chem.*, **A166**, 59 (1933).



(7-62)

The incorrect use[152] of this reaction to show that the hypophosphate anion has the structure which we now attribute to the isohypophosphate anion exemplifies the fact that it is a risky business to assign structures on the

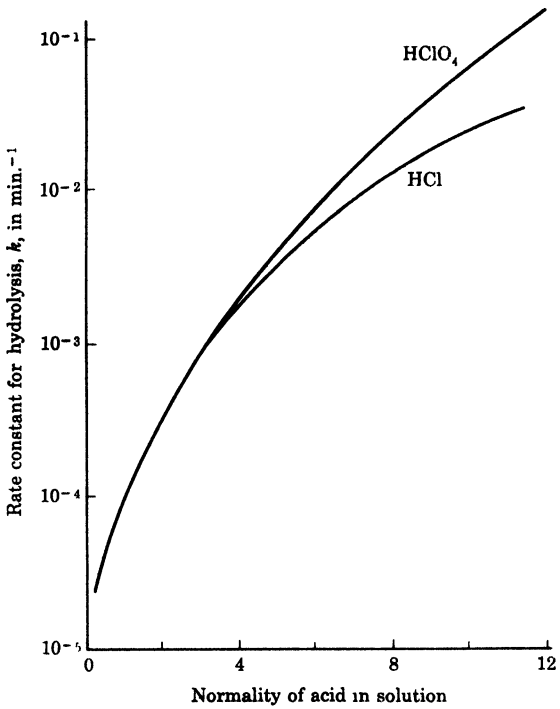
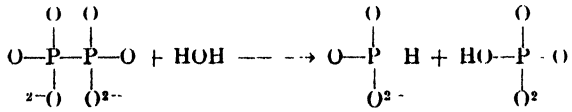


Fig. 7-9 Hydrolysis of the hypophosphate ion in acidic solutions at 40°C

basis of over-all chemical reactions. Indeed, it is the structure of the activated complex and not of the gross reactants which determines the course of a reaction. It would be interesting to carry out a detailed kinetic study of reaction 7-62 for the purpose of defining the activated complex, in which the *d*-orbitals of the phosphorus atom probably allow formation of the oxygen bridge before the P—P bond is broken.

The hydrolysis of the hypophosphate anion proceeds according to the following equation:



(7-63)

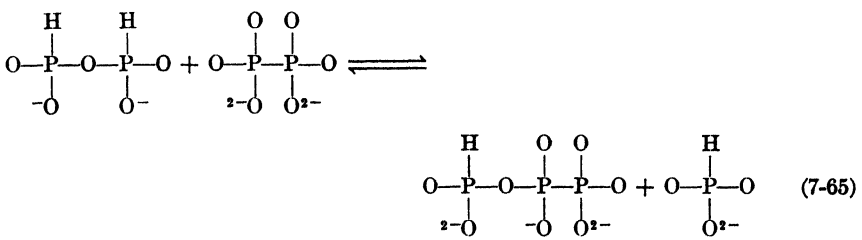
Because the rate of hydrolysis is quite slow at room temperature but is catalyzed by acid, the reported hydrolysis studies[145,146] have been carried out in acid media. An example of the variation of the hydrolysis rate with concentration of added strong acid is given in Figure 7-9. The available data indicate that the half-life of the hypophosphate anion with respect to hydrolysis is 180 days in 1 *N* acid at 25°C. The activation energy is roughly estimated to be 20–25 kcals./mole. Radioactive exchange data[158] show that equation 7-63 does not correspond to a measurable equilibrium at room temperature in concentrated acid. The equilibrium constant corresponding to equation 7-63 must be greater than 1.2×10^4 mole/l.

Proof that the menthyl ester of hypophosphoric acid is truly such an ester is obtained by division[138] of this ester into the free acid and menthene.

$$(C_{10}H_{19}O)_4P_2O_2 \xrightarrow{\Delta} (HO)_2(O)PP(O)(OH)_2 + 4\ C_{10}H_{18} \qquad (7\text{-}64)$$

Lower Oxyacids of Greater Complexity

By means of an exchange process which he calls interanhydrization, Blaser[123] has prepared several oxyacids of phosphorus containing three phosphorus atoms. The acid in this category which has been the most carefully investigated is obtained by combining the pyrophosphate and hypophosphate ions, as shown by the following equation:

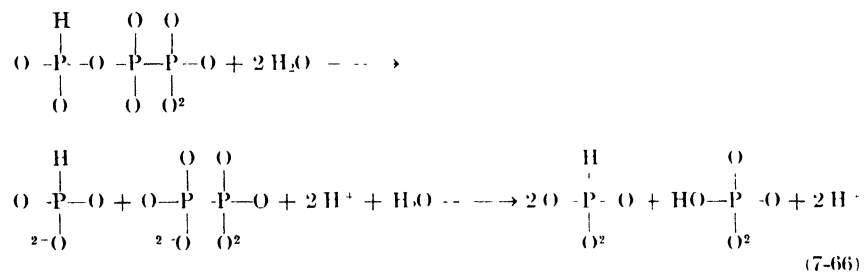


(7-65)

After boiling concentrated solutions of sodium pyrophosphate with sodium hypophosphate for 5–10 min., the excess reagents and the expected salts formed by hydrolysis were removed by suitable methods, and a sodium salt was then isolated by repeated precipitation with alcohol. This

[158] J. N. Wilson, *J Am. Chem. Soc.*, **60**, 2697 (1938). For a misinterpretation of the data, see R. Daudel, *Compt rend.*, **215**, 177 (1942).

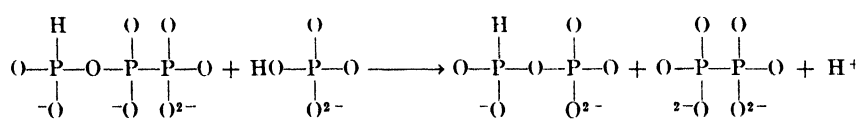
sodium salt, which appeared as an oil, gave two inflection points on being titrated with acid. The first inflection point at pH 5.1 corresponded to a Na/P mole ratio of 1.00, and the second inflection point at pH 9.6 corresponded to Na/P of 1.66. Proof that this was a pure compound was obtained by chromatography in an alkaline media in which a single spot was found. This spot moves somewhat faster than the spot for the hypophosphate ion. Chromatography in acid media resulted in hydrolysis to give the two spots corresponding to orthophosphorous and hypophosphoric acids. This new anion based on three phosphorus atoms undergoes hydrolysis very slowly in neutral solution and rapidly in the presence of acid or base. In basic or mildly acidic solution, the orthophosphite and hypophosphate anions are obtained as indicated by the first step in equation 7-66.



(7-66)

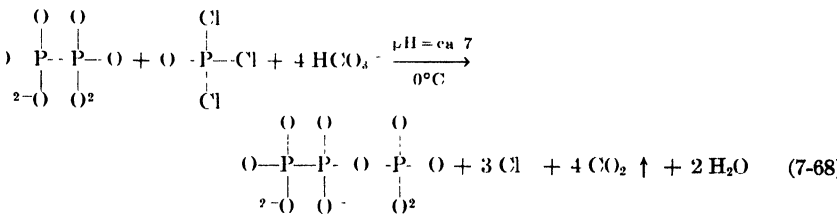
The second step in this equation corresponds to complete hydrolysis in strong acid. The final products are then two moles of orthophosphite to one mole of orthophosphate. The half-life with respect to hydrolysis of the original anion (based on three phosphorus atoms) is found to be approximately 100 min. at 0°C. in 0.5 *N* NaOH. It should also be noted that this new anion is not oxidized by iodine in sodium bicarbonate solution at room temperature.

This new anion based on three phosphorus atoms can also enter into interanhydrization reactions. Thus, when it is combined with an equimolar amount of orthophosphate anion in neutral solution, there is, according to Blaser,[123] a good yield of an equimolar mixture of the isohypophosphate and hypophosphate anions as indicated by equation 7-67.



(7-67)

A different oxyacid based on three phosphorus atoms has been prepared[123] by adding phosphorus oxychloride to a hypophosphate solution buffered with bicarbonate.



(7-68)

Although this second new anion has not been so well characterized as the anion described in the previous paragraph, it is found to be quite stable to the oxidizing action of bromine in sodium bicarbonate solution. This relative inertness differentiates it from the parent hypophosphate anion which is rapidly oxidized under the same conditions. The chromatographic studies by Thilo and Heinz[124] on the hydrolysis products of phosphorus tribromide and triiodide also gave evidence of the existence of an anion based on three or four phosphorus atoms and containing at least one P—O—P and one P—P linkage per molecule-ion. There are also several rather old-fashioned Russian papers[159] which give some data on salts of lower oxyacids which probably are based on several phosphorus atoms. Thus, for example, two silver salts having the following empirical compositions are described: $Ag_8H_5P_4O_{16} = 8\,Ag_2O \cdot 5\,H_2O \cdot 2\,P_2O_3 \cdot P_2O_5$ and $Ag_{11}H_3P_4O_{16} = 11\,Ag_2O \cdot 3\,H_2O \cdot P_2O_3 \cdot 3\,P_2O_5$.

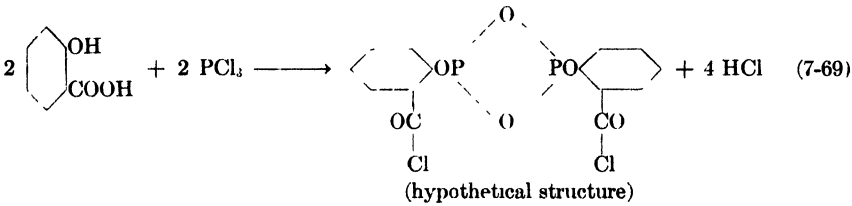
A "metaphosphorous acid," with an empirical formula of HPO_2, has been described in the literature as resulting from burning dry phosphine in dry oxygen.[111] If the observed crystalline material really exhibited the formula HPO_2, it is probably an un-ionized substance (which should, thus, not be called an acid) having a structure like the one shown in item 3 of series 7-38.

Esters of "metaphosphorous" acid, having an empirical formula RPO_2, and esters of "metaphosphonic acid," which are sometimes called "phosphonous anhydrides" and also have the formula RPO_2, have been obtained as crystalline products.[5] The aryl metaphosphites which have been made[160]

[159] V. N. Osipov, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 933, 941 (1936); also see V. N. Osipov and A. S. Titova, *ibid.*, **6**, 1559 (1936), and I. V. Bussen and V. V. Soboleva, *Uchenye Zapiski Leningrad. Gosudarst. Univ. A. A. Zhdanova*, **1939**, No. 7, 34, 10.

[160] R. Anschutz, E. Schroeder, E. Weber, and R. Annspach, *Ann.*, **346**, 300 (1906); R. Anschutz, A. Robitsek, and F. Schmidt, *ibid.*, **346**, 335 (1906); R. Anschütz and A. Robitsek, *ibid.*, **346**, 311 (1906); R. Anschütz and H. Mehring, *ibid.*, **346**, 315 (1906); R. Anschutz and R. Annspach, *ibid.*, **346**, 380 (1906); R. Anschütz, *Ber*, **30**, 221 (1897); R. Anschütz and W. O. Emery, *Ann.*, **239**, 301 (1887).

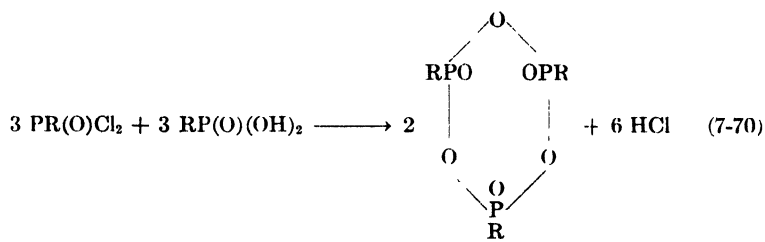
are all derivatives of salicylic acid and are obtained by heating an excess of phosphorus trichloride with salicylic acid or a substituted salicylic acid in boiling xylene.



(hypothetical structure)

It should be noted that in equation 7-69 the aryl metaphosphite is shown as a ring compound containing two phosphorus atoms. This is not necessarily the case, but it is presented as an example of the type of structure to be expected if the substance is truly a metaphosphite.

With the exception of the isoamyl ester, all of the metaphosphonates which have been prepared are aryl derivatives [119,161] They have been made by heating phosphonyl dichlorides with the corresponding primary phosphonic acid, usually in benzene solution according to the following equation. Again, the products, which are isolated by crystallization in the absence of moisture, are assigned a ring structure here, although there is no physical evidence available as to their real constitution.



(hypothetical structure)

Nomenclature of Lower Oxyacids Based on Several Phosphorus Atoms

The "hypophosphate" and "pyrophosphite" names are old and quite well accepted. However, the use of "isohypophosphate" is undesirable because hypophosphoric acid has one more acidic hydrogen than does the iso acid. The term "diphosphite" is a harmless name with nothing in particular to commend it and with no outstanding disadvantages. The real problem comes in naming anions based on three or more phosphorus

[161] F. Guichard, *Ber.*, **32**, 1572 (1899); A. Michaelis, *Ann.*, **293**, 193 (1896); *ibid*, **294**, 1 (1896); A. Michaelis and F. Rothe, *Ber.*, **25**, 1747 (1892).

atoms In this case the name should indicate the following: (1) the number of phosphorus atoms per anion, (2) the number of hydrogen atoms directly attached to phosphorus and which phosphorus atom they are attached to, and (3) the number and position of P—P bonds as compared to P—O—P linkages.

These requirements are met by the coordination-compound system of nomenclature which is briefly described on pp. 90-91. By this system, the pyrophosphites, diphosphites, isohypophosphates, and hypophosphates are known respectively as 1,2-dihydrotetroxy-μ-oxodiphosphates, hydropentoxydiphosphates, hydropentoxy-μ-oxodiphosphates, and hexoxydiphosphates. The anion based on three phosphorus atoms which is shown in equation 7-65 is named 1-hydroseptoxy-*ina*-[1-μ-oxotriphosphate], and the un-ionized ring structure in equation 7-70 would be 1,2,3-trialkyl-1,2,3-trioxy-*cyclo*-[tri-μ-oxotriphosphorus].

Analytical Procedures

Although analysis of the pure lower oxyacids of phosphorus and their derivatives is a relatively simple matter for which new procedures are continually being developed,[162] the problem of assaying mixtures of these acids is fraught with many difficulties and did not receive a satisfactory solution until the last few years. The classical approach to the problem is based on the fact that, under certain conditions, one acid will be readily oxidized and another will not. Preferential oxidation with halogens,[163] particularly iodine, has been the basis of a number of procedures for differential analysis. Other oxidizing agents such as iodic acid,[164] the selenite and tellurite[165] ions, and ceric[166] ion have also been employed in differential assays. In addition, potentiometric titrations have been employed to some extent in the assay of mixtures of the lower oxyacids of phosphorus.[167] The wet-chemi-

[162] Recent work on colorimetric procedures for the hypophosphite ion has been described by A. P. Scanzillo, *Anal. Chem.*, **26**, 411 (1954) and G. Gutzeit, U. S. Pat. 2,697,651 (1954, assigned to General American Transportation Co.).

[163] L. Wolf and W. Jung, *Z. anorg. u. allgem. Chem.*, **201**, 353 (1931); D. Raquet and P. Pinte, *J. pharm. chim.*, **18**, 5 (1933); *ibid*, **18**, 90 (1933); R. T. Jones and E. H. Swift, *Anal. Chem.*, **25**, 1272 (1953).

[164] A. Brukl and M. Behr, *Z. anal. Chem.*, **64**, 23 (1924).

[165] W. Jung, *Anales asoc. quím. argentina*, **29**, 101 (1941); *ibid.*, **30**, 65 (1942); *Anales soc. cient. argentina*, **132**, 201 (1941).

[166] B. N. Bernhart, *Anal. Chem.*, **26**, 1798 (1954).

[167] L. Wolf and W. Jung, *Z. anorg. u. allgem. Chem.*, **201**, 347 (1931); W. Grundmann and R. Hellmich, *J. prakt. Chem.*, **143**, 100 (1935); R. Paris and P. Tardy, *Compt. rend.*, **223**, 1001 (1946)

cal procedures for the determination of hypophosphites, orthophosphites, hypophosphates, and orthophosphates alone and in various mixtures have been reviewed by several authors.[168]

Although it has only been used for a very few years, paper chromatography has been found to be an extremely useful tool in separating and

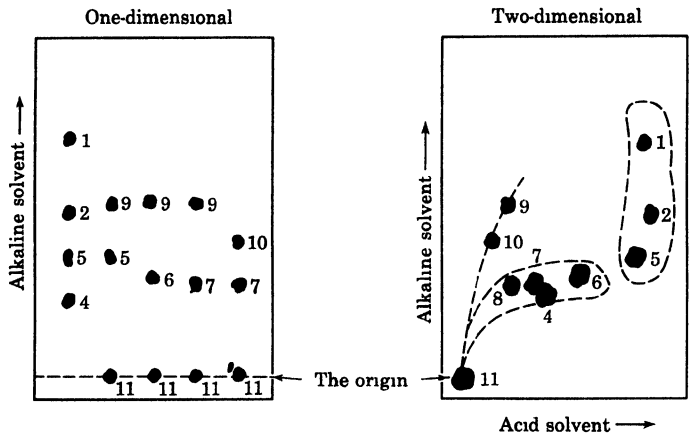


Fig. 7-10. Examples of one- and two-dimensional chromatograms of mixed oxyacids of phosphorus. The various anions studied were (1) hypophosphite, (2) orthophosphite, (3) pyrophosphite, (4) hypophosphate, (5) orthophosphate, (6) pyrophosphate, (7) tripolyphosphate, (8) tetrapolyphosphate, (9) trimetaphosphate, (10) tetrametaphosphate, (11) long chain polyphosphate The alkaline solvent was 40 ml isopropanol, 20 ml. isobutanol, 1 ml. ammonia (22° Bé soln.), and 39 ml. water The acid solvent was used after the alkaline solvent in the two-dimensional work. It consisted of 80 ml. ethanol, 5 g. trichloroacetic acid, 0.3 ml. ammonia (22° Bé), and 20 ml water.

determining mixtures of the oxyacids of phosphorus.[124,123,169] Thus, Ebel[169] and coworkers have demonstrated that hypophosphite, phosphite, hypophosphate, and orthophosphate can be readily separated on a one-dimensional chromatogram, as shown in Figure 7-10. It should be noted that in the two-dimensional chromatogram shown in the same figure, the oxyacids of phosphorus appear to lie in three major groups: (1) acids based on a

[168] R. Klement, *Handbuch der analytischen Chemie*, eds. W. Fresenius and G. Jander, Springer, Berlin, 1953, Sect. 3, Vol. Vaβ, pp. 323–31 (phosphites), 331–40 (hypophosphites), and 340–48 (hypophosphates); W. M. Hartmann, *Z. anal. Chem.*, **97**, 273 (1934); T. A. Kryukova, *Zadvodskya Lab.*, **6**, 47 (1937).

[169] J. P. Ebel, *Mikrochim. Acta*, **1954**, 679; Y. Volmar, J. P. Ebel, and Y. Fawzi Bassili, *Bull. soc. chim. France*, **1953**, 1085; Y. Volmar, J. P. Ebel, and F. B. Yacoub, *Compt. rend.*, **235**, 372 (1952); A. Bonnin and P. Sue, *Compt. rend.*, **234**, 960 (1952).

single phosphorus atom, which appear to the far right on the chromatogram when aligned as shown in Figure 7-10; (2) acids exhibiting a chain structure, which appear in a region between the origin and the acids based on a single phosphorus—with the larger members of a given homologous series being closer to the origin; and (3) acids having a ring structure, which lie to the left of the chains. Unfortunately, the only ring acids known at present are phosphates, so it is not possible to state with certainty that ring derivatives of the lower oxyacids will form a series lying to the left of

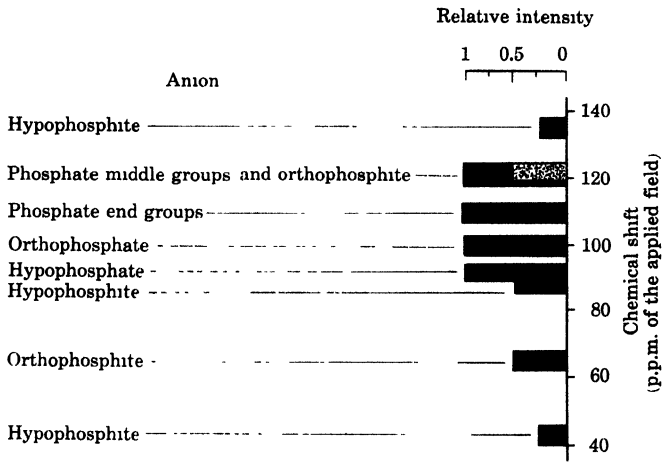


Fig. 7-11 Schematic diagram of the placement and relative intensity of the P^{32} nuclear magnetic resonance peaks in a mixture of oxyacids of phosphorus. For any given species the height of a given resonance peak is proportional to the amount of phosphorus present. The chemical shift of the orthosphosphate ion was arbitrarily chosen as 100 p.p m. of the applied magnetic field

their chain equivalents. Paper electrophoresis has also been used in separating the oxyacids of phosphorus, including the lower acids.[170]

Another very promising but less well developed new analytical tool for the quantitative differential determination of the various oxyacids of phosphorus in the presence of each other is found in nuclear magnetic resonance.[171] In Figure 7-11, the anions of the various common oxyacids of phosphorus are listed in the order of their chemical shift. The intensity factor plotted in this figure indicates the relative area (and to a rough

[170] R. Klement and H. Frieser, *Angew. Chem.*, **66**, 138 (1954).

[171] C. F. Callis, J. R. Van Wazer, and J. N. Schoolery, *Anal. Chem.*, **28**, 269 (1956); *J. Am. Chem. Soc.*, **77**, 4945 (1955).

approximation, the height) of the resonance peak for equal numbers of phosphorus atoms. Thus, at equimolar concentrations the hypophosphite peak at a shift of 133 p.p.m. is only one-quarter the area of the orthophosphate peak appearing at a shift of 100 p.p.m. under the same experimental conditions. Even though the peak for phosphate middle-units and one of the peaks for orthophosphite exhibit the same chemical shift of 120 p.p.m., it is possible to determine both of these species in a mixture by using the second orthophosphite peak at 64 p.p.m. to determine the relative amount of the condensed phosphate middle-units by subtracting the orthophosphite from the 120 p.p.m. peak. The other case of a combination of acids covered in Figure 7-11 in which interference is possible is between the hypophosphate and hypophosphite anions; but here again another peak for the hypophosphite at either 42 or 133 p.p.m. can be used.

As more and more oxyacids of phosphorus are discovered, it will probably be necessary to use a combination of paper chromatography and nuclear magnetic resonance to identify the constituents in mixtures. It is predicted that, in differential assays of the future, the oxyacids of phosphorus will be primarily characterized by a combination of ion exchange or paper chromatography with nuclear magnetic resonance. In addition, preferential oxidations followed by reapplication of these same analytical procedures may also be employed in especially difficult cases.

CHAPTER 8

Structure and Properties of the Condensed Phosphates

HISTORY

Berzelius[1] in 1816 found that, when ordinary phosphoric acid is ignited, the product is fundamentally different from orthophosphoric acid in that it acquires the power of coagulating a solution of albumen. In 1828, Clark[2] again prepared sodium pyrophosphate as first made by Berzelius and observed with surprise that he obtained a white and not a yellow precipitate with silver nitrate. The most outstanding early paper in this field was written by Thomas Graham,[3] and in it he classed all phosphates into three groups: the orthophosphates, the pyrophosphates, and the metaphosphates—a classification which was advanced for its day, but which has led to considerable confusion in the literature of the last fifty years concerned with phosphates. The ortho-pyro-meta notation is based on the old "double oxide" formulation of Berzelius, in which salts of the oxyacids are written in terms of their oxides. Thus, we have the following series of acids, which in 1833 was a demonstration of the law of multiple proportions. Both this law and the concept of acids, bases, and salts were leading subjects at that period in the development of chemistry.

Orthophosphoric acid	$3\ H_2O \cdot P_2O_5 \backsimeq H_3PO_4$
Pyrophosphoric acid	$2\ H_2O \cdot P_2O_5 \backsimeq H_4P_2O_7$
Metaphosphoric acid	$H_2O \cdot P_2O_5 \backsimeq HPO_3$

Fleitmann and Henneberg[4] introduced the idea of polyphosphoric acids derived from ordinary phosphoric acid by abstraction of water, and they

[1] J. J. Berzelius, *Ann. Physik*, **53**, 393 (1816); *ibid.*, **54**, 31 (1816); *Ann. Chim. Phys.*, **2**, No. 2, 151, 217, 329 (1816).

[2] T. Clark, *Edinburgh J. Sci.*, **7**, 298 (1827).

[3] T. Graham, *Phil. Trans*, **123**, 253 (1833); *Ann. Physik*, **32**, 33 (1834).

[4] T. Fleitmann and W. Henneberg, *Liebig's Ann*, **65**, 30, 387 (1845).

and other early authors described some of these salts. Thus, the following series was set up:

Orthophosphoric acid, H_3PO_4	H_3PO_4
Pyrophosphoric acid, $H_4P_2O_7$	2 H_3PO_4 less H_2O
Triphosphoric acid, $H_5P_3O_{10}$	3 H_3PO_4 less 2 H_2O
Tetraphosphoric acid, $H_6P_4O_{13}$	4 H_3PO_4 less 3 H_2O
Etc.	Etc.

The general equation of the above series is $mH_3PO_4 - (m - 1)H_2O$; and it can be seen that, when m approaches infinity, the formula becomes $(H_3PO_4 - H_2O)_m = (HPO_3)_m$, which is the metaphosphoric acid of Graham. Soon after Fleitmann and Henneberg's papers appeared, it was argued by some that the polyphosphates intermediate between the pyro- and metaphosphates were simply mixtures of these two end members of the series. Unfortunately, due to lack of critical experimental techniques, the debate as to whether or not polyphosphates other than the pyrophosphate really exist lasted until very recently, when it was shown quite conclusively that tri-[5] and tetraphosphates[6] can be crystallized, and that higher homologues can be separated.[7] The result of this century-long controversy has been that most chemists (such as the authors of general inorganic texts) until the last few years have chosen the superficially simple—but, alas, incorrect—meta-pyro-mixture notation for use in describing polyphosphates. Such ortho-meta-pyro notation is still occasionally found, especially in the technological literature.

The region between pure phosphorus pentoxide and the metaphosphate composition was not investigated until 1912.[8] Following Kroll, we shall call this composition range the ultraphosphate region. Even at the present time, the ultraphosphate region has received very little study even though, as will be shown later in this chapter, a complex system of various structures is to be expected in this region.

The term "condensed phosphates" covers the pyro-, meta-, poly-, and ultraphosphates. It is, in fact, a generic title for all phosphates, the acids of which have less water than orthophosphoric acid: $3\ H_2O \cdot P_2O_5$. The pyro-, meta-, and polyphosphates are often also called "molecularly dehy-

[5] E. P. Partridge, V. Hicks, and G. W. Smith, *J. Am. Chem. Soc*, **63**, 454 (1941).

[6] O. T. Quimby, *J. Phys. Chem.*, **58**, 615 (1954); R. P. Langguth, R. K. Osterheld, and E. Karl-Kroupa, *ibid.*, **60**, 1335 (1956); R. K. Osterheld and R. P. Langguth, *ibid.*, **59**, 76 (1955).

[7] J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 647 (1950); also see J. Crowther, *Anal Chem.*, **26**, 1383 (1954); and A. E. Westman and J. Crowther, *J. Am. Ceramic Soc.*, **37**, 420 (1954).

[8] A. V. Kroll, *Ueber Ultraphosphate*, Thesis, Univ of Leipsig, 1912

drated" phosphates, with reference to the common procedure of dehydrating acid orthophosphates, as in the following equation:

$$2\ Na_2HPO_4 \xrightarrow{\Delta} Na_4P_2O_7 + H_2O$$

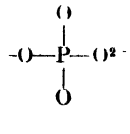
disodium orthophosphate — tetrasodium pyrophosphate

In the period from 1833 to the present, a large number of technical articles were written about the number of condensed phosphates which have been thought to exist and the structure of these compounds. However, it was not until the middle of the 20th century (1945–1953) that the problem of the number and kind of condensed phosphates was solved in its broad outlines. Before this time, the field was truly chaotic. One of the main reasons for this state of confusion was that no analytical techniques were available for adequately differentiating between the various condensed phosphates. In addition, the growth of chemical theory, since the inception of quantum mechanics in 1925, finally necessitated an approach to the structure of phosphates which would bring them in line with general chemical theory.

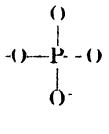
BASIC PRINCIPLES OF PHOSPHATE STRUCTURES[9]

As in the large majority of its compounds, phosphorus exhibits sp^3-bonding (four-fold coordination number with tetrahedral symmetry) in the phosphates. By definition, the phosphates are those compounds of phosphorus in the anions of which each atom of phosphorus is surrounded by four oxygen atoms arranged at corners of a tetrahedron. By sharing oxygen atoms between tetrahedra, chains, rings, and branched polymers of interconnected PO_4 tetrahedra can be produced. This means that there are only several building blocks from which phosphates can be made. One of them is the PO_4 group in which three oxygen atoms are shared with neighboring PO_4 groups. This is called a "branching point." Another is the PO_4 group in which two oxygen atoms are shared with neighboring groups, and there is one negative charge (counterbalanced by a cation) or ester linkage. This is called a "middle PO_4 group." Then, we have the "end PO_4 group" in which one oxygen is shared, and there are two negative charges or ester linkages. Finally, there is the single (ortho- or monophosphate) PO_4 group in which there are three negative charges or ester linkages. These units, other than the orthophosphate, are shown below, along with their descriptive names. The units depicted below are the building blocks from which more or less complicated molecules or molecule-ions are formed.

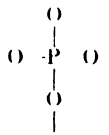
[9] J. R. Van Wazer and E. J. Griffith, *J. Am. Chem. Soc.*, **77**, 6140 (1955).



end group

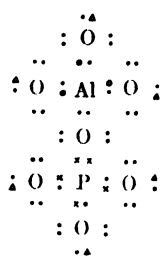


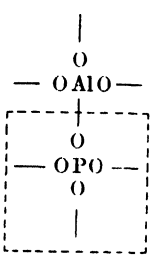
middle group



branching point

There is an additional structural unit, the "four-way branching point," which can appear in anionic or neutral structures based on phosphorus plus an electron-pair-acceptor atom. Thus, the mixed phosphate-borates or phosphate-aluminates can exhibit a four-way branching point as indicated below by the electronic and bond notations (π-bonding not shown, as usual).





four-way branching point

where ^{x} = electrons from P, $^{\bullet}$ = electrons from O, ^{o} = electrons from Al, and $^{\Delta}$ = electrons obtained from the ionization of the counter-ions or from bonds with atoms not shown.

By putting two end groups together, we obtain the pyrophosphate molecule-ion, $P_2O_7^{4-}$; and by adding middle groups between the end groups, we obtain a whole series of straight chain molecule-ions. Middle groups can also be connected to each other to give ring molecule-ions. Branching points can be used to make branched chains or to hook chains onto rings. They can also be used to form fused-ring structures and a large variety of complex three-dimensional structures. It should be noted that any form of phosphorus pentoxide must be completely made from branching points, and therefore the various structures corresponding to $(P_2O_5)_n$ should be considered as limiting cases of the system of phosphates.

In a recent study by nuclear magnetic resonance of the chemical bonding in phosphates,[10] it was found that there is a measurable difference between the various types of PO_4 groups—a difference which seems to be attributable in great part to a variation in the distribution of π-bonding. This study

[10] J. R. Van Wazer, C. F. Callis, and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 4945 (1955). J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956)

showed that a middle group in a chain is equivalent to a middle group in a ring, and that the end groups have the same P—O bonding characteristics regardless of the length of the chain.

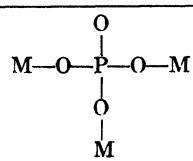
Now, if we let M stand for one equivalent of any cation or organic radical, all phosphates may be written as $xM_2O \cdot yP_2O_5$, where M_2O may stand for a mixture of different cationic oxides in a given compound. Now, by letting R equal M_2O/P_2O_5, we find that $R = 3$ corresponds to the orthophosphate and $R = 0$ corresponds to the phosphorus pentoxide. In between these two limits, we have the polyphosphate region, for which $1 < R \leqslant 3$, the metaphosphate composition for which $R = 1$, and the ultraphosphate region for which $0 < R < 1$. It should be noted that for the purposes of this discussion, the orthophosphate and pyrophosphate ($R = 2$ for pyro) are considered as parts of the polyphosphate region. Phosphates in which $R > 3$ must be considered as mixed salts, since the charge on a single PO_4 group can only counterbalance three equivalents of cation. Such a crystalline salt for which $R > 3$ is hilgenstockite, or tetracalcium phosphate, with the formula $4\ CaO \cdot P_2O_5$. This must be considered as the double salt $(3\ CaO \cdot P_2O_5)CaO$. In this discussion, only the PO_4 groups and their counter ions are considered; other ions in complicated crystal structures are ignored.

Combinations of PO_4 Groups

By combining end groups, middle groups, and branching points in all possible ways and ignoring the effects of steric hindrance and strain, a large number of hypothetical phosphate formulas can be derived.

In the case of a single PO_4 group, there is, of course, just one arrangement, that of the orthophosphate ion shown in Table 8-1. It should be noted that the ionization of the M constituent is not depicted. When the M—O bond is highly ionic, such as in the case of M being the tetramethylammonium ion, the dissociation is complete, but for esters the M—O bond is essentially covalent. Since the orthophosphate ion or radical is the only example in the family of phosphates of a single isolated PO_4 group, and all other

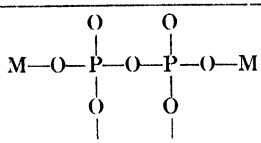
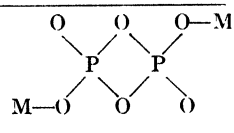
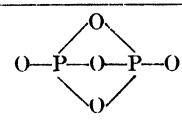
TABLE 8-1
The Monophosphate

	Orthophosphate, M_3PO_4 (Numerous crystalline and amorphous examples)

phosphates are made up of interconnected PO_4 groups, it is apparent that the term "condensed phosphates" is very fitting for all phosphates except the orthophosphate.

In the case of two PO_4 groups, there are three possible arrangements which are depicted below in Table 8-2. Only one of these three, the pyrophosphate anion, is known. The other two structures involve considerable strain and have not been proved to exist, although many authors have hypothesized a dimetaphosphate, $(MPO_3)_2$, on the basis of insufficient or improperly interpreted evidence. These dimetaphosphates have been shown to be misnamed and to consist of other compounds. There also is no basis for believing in the existence of a monomeric form of P_2O_5, which would be highly strained and hence abnormally reactive and difficult, if not impossible, to produce and retain. Monomeric P_2O_5, if once made, would be expected to rearrange to a more stable form (*e.g.*, the dimer of the empirical formula) except at very low temperatures.

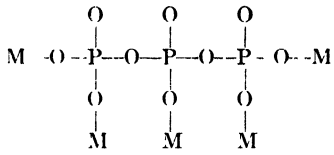
TABLE 8-2
The Diphosphates

		
Pyrophosphate, $M_4P_2O_7$ (Numerous crystalline and amorphous examples)	Dimetaphosphate, $(MPO_3)_2$ (Not known)	Monomeric phosphorus pentoxide (Not known)

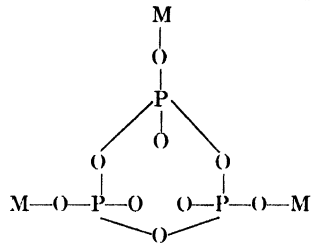
Now we find that there are four ways in which three PO_4 groups can be connected. These four structures are shown in Table 8-3. The linear structure, called the tripolyphosphate anion, is well known, and so is the simple ring structure called the trimetaphosphate anion. The other two structures, which involve dimetaphosphate bridges, have not been shown to exist, probably because of the large strain which occurs in the dimetaphosphate bridge. It should be noted that one of these structures has the formula of a trimetaphosphate, and the other one is an ultraphosphate.

There are eleven different ways in which four PO_4 groups, as shown in Table 8-4, can be put together. Of these, only three structures—the tetrapolyphosphate, the tetrametaphosphate, and dimeric phosphorus pentoxide—have been shown to exist in crystalline form. Also the ultraphosphate structure, labeled compound G, must have at least a momentary existence in the hydrolysis of the P_4O_{10} molecule (shown as compound J). Com-

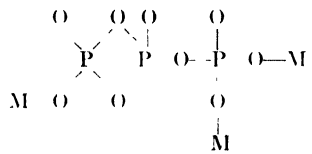
TABLE 8-3
The Triphosphates



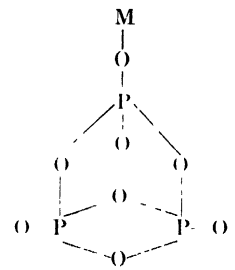
Tripolyphosphate, $M_5P_3O_{10}$
(Some crystalline examples known)



Trimetaphosphate, $(NPO_3)_3$
(Structure of sodium salt shown by x-ray and hydrolysis)



"Iso" trimetaphosphate, $(MPO_3)_3$
(Not known)



An ultraphosphate, MP_3O_8
$= M_2O \cdot 3\,P_2O_5$
(Not known)

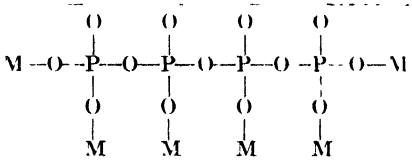
pounds B, D, G, and J, a tetrapoly-, tetrameta-, ultraphosphate, and phosphoric anhydride, respectively, exhibit branching points; there is, however, no strain in these structures. Compounds E, F, H, I, and K all have dimetaphosphate rings which are under considerable strain.

This system of building up phosphate structures can be continued, but it is apparent that the number of possible structures begins to increase very rapidly as the number of PO_4 groups is raised from four to five to six to seven, etc. A tabulation of the types of structures made by combining from one to six PO_4 groups into molecule-ions is given in Table 8-5.

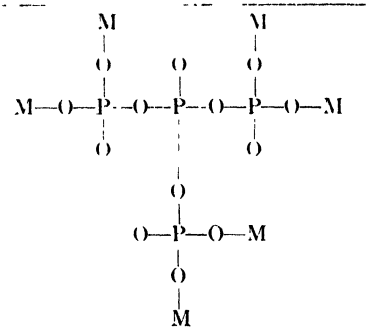
Strain in P—O—P Linkages

The question of the possible existence of dimetaphosphate rings in phosphate molecule-ions and molecules is an interesting one. The largest bond angles are obtained when this ring is planar. In this case, the four bond

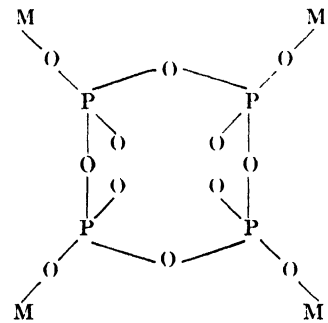
TABLE 8-4
The Tetraphosphates



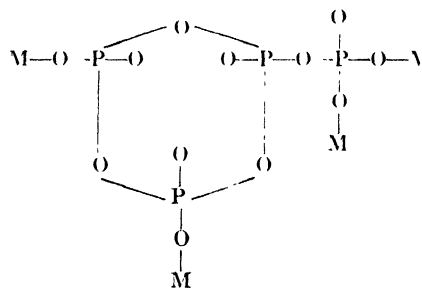
(A) Tetrapolyphosphate, $M_6P_4O_{13}$
(Crystallized as barium and lead salts; also shown to exist by chromatography)



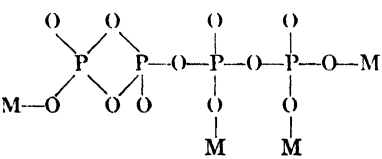
(B) "Iso" tetrapolyphosphate, $M_6P_4O_{13}$
(Not known)



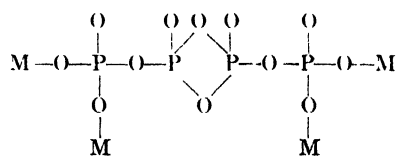
(C) Tetrametaphosphate, $(MPO_3)_4$
(Structure of aluminum and ammonium salts shown by x-ray)



(D) "Iso" tetrametaphosphate, $(MPO_3)_4$
(Not known)



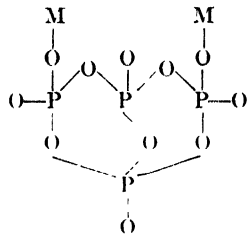
(E) "Iso" tetrametaphosphate, $(MPO_3)_4$
(Not known)



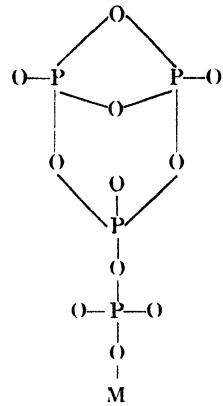
(F) "Iso"tetrametaphosphate, $(MPO_3)_4$
(Not known)

angles must add up to 360°, which is considerably smaller than the angle for the sp^3-hybridization of the phosphorus atom and the usual hybridizas tion of the oxygen atom which lies between p^2 and sp. Since two angles having a minimum value of 90° for the p^2-hybridization of oxygen plus two 109°28′ angles for the sp^3-hybridization of phosphorus equals 398°56′, the angular strain in the ring will be no less than 39° in this case. On the

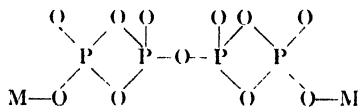
TABLE 8-4 (*continued*)



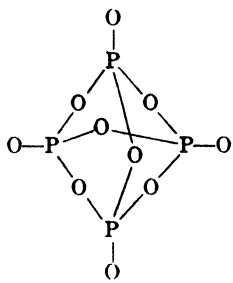
(G) An ultraphosphate, $M_2P_4O_{11}$ = $M_2O \cdot 2\ P_2O_5$
(Must appear as transient intermediate in hydrolysis of P_4O_{10})



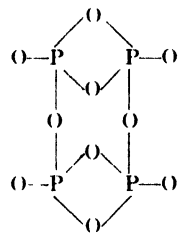
(H) An ultraphosphate, $M_2P_4O_{11}$ = $M_2O \cdot 2\ P_2O_5$
(Not known)



(I) An ultraphosphate, $M_2P_4O_{11}$ = $M_2O \cdot 2\ P_2O_5$
(Not known)



(J) Dimeric phosphorus pentoxide, $(P_2O_5)_2$
(Structure of vapor and hexagonal crystalline forms of phosphorus pentoxide)



(K) An isomer of dimeric phosphorus pentoxide, $(P_2O_5)_2$
(Not known)

other hand, if the P--O P angle is near the average value of about 140° and the O--P O angle is only 100°, the sum of the angles would be about 100° larger than the sum of the angles in a planar dimetaphosphate ring.

TABLE 8-5
The Phosphate Family

P atoms per unit molecular structure	Total number of computed structures	Number of isolated known structures	"Polyphosphates" Number of chain compounds		"Metaphosphates" Number of ring compounds			"Ultraphosphates" Number of crosslinked compounds	
					Simple,[a] excepting dimeta rings	Substituted			
			Straight[a]	Branched		Excepting dimeta rings	With dimeta rings	Excepting[a] dimeta rings	With dimeta rings
1	1	1	(1)	0	0	0	0	0	0
2	3	1	1	0	0	0	1	0	1
3	4	2	1	0	1	0	1	0	1
4	11	3	1	1	1	1	2	2	3
5	26	2	1	2	1	3	3	7	9
6	ca. 74	2	1	4		8	6	ca. 18	ca. 36

[a] Includes all compositions to be expected from present methods of synthesis

Comparison[11] of the calculated bond energies with the available experimental data on cyclopropane, cyclobutane, ethylene oxide, and the P_4 molecule indicates that the heat of formation of phosphates containing dimetaphosphate rings will be raised by only a few kilocalories per mole of dimeta rings.

In addition to the dimetaphosphate ring in which two corners of adjacent PO_4 tetrahedra are shared, there is the case in which three corners of one tetrahedron are shared with the three corners of a neighboring tetrahedron. There is only one compound– a diphosphate—which can show this structure, and this is monomeric P_2O_5, a compound which has never been isolated. In the structure of monomeric P_2O_5, the O—P—O angle, which we shall call 2α, is related to the P—O—P bond angle, which we shall call 2β, by the equation.

$$\sin \alpha = \cos 30^\circ \cos \beta \tag{8-1}$$

If the P—O—P and O—P—O bond angles were equal ($\alpha = \beta$) this equation gives a value of 82° for the angles This corresponds to a very large amount of strain in the monomeric P_2O_5 molecule

By the use of present methods of synthesis for phosphates, in which reorganization at high temperatures is involved, it will be impossible to produce structures exhibiting dimetaphosphate rings or to produce monomeric P_2O_5. If these structures were to be made at moderately high temperatures or above, they would immediately disappear by reorganizing to other structures which do not exhibit strain and hence are more stable. However, the use of positional synthesis procedures of the type employed in organic chemistry should result in the closure of dimetaphosphate rings, which ought to be reasonably stable at normal temperatures or below.

Theory of Linkages in Phosphates[9]

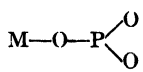
If we either neglect ionization or consider an M^+, ^-O ^-P arrangement as a linkage of the ionic type, we can compute the total number of linkages in a given phosphate composition. A linkage may be of two kinds: a P—O—P linkage or an M—O—P linkage. Since there are three bonds (ionic or covalent) proceeding from each PO_4 group, and since there is only one from each M, the total number of linkages, N_t, is given by

$$N_t = (M + 3P)/2 \tag{8-2}$$

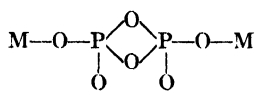
[11] Heats of formation for the cyclic hydrocarbons are calculated from data given by L. Ruzicka, *Chemistry & Industry*, **54**, 2 (1935). The ethylene oxide and P_4 values come from *Natl. Bur. Standards* (*U. S.*), *Circ.*, **500**, 122, 72 (1952). The calculation of unstrained bond energies is based on M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953) Effect of strain on the heats of formation is then 16 kcal. for C_3H_6, 8 kcal. for C_4H_8, 0 kcal for C_2H_2O, and 12 kcal for P_4

N_t must be an integer and, if it is not, one must double the number of atoms in the proposed compounds in order to obtain the simplest structure which can exist. For example, there is no phosphate in which there is only one phosphorus atom and two cations (R = M/P = 2/1 = 2), but there is a known compound containing two phosphorus and four cations (R = 4/2 = 2). This point is easily demonstrated by substituting the values into equation 8-2.

It may be seen that the number of phosphorus atoms in the simplest phosphate structure having a given M_2O/P_2O_5 (= M/P) ratio, R, is found when the sum of the numerator and denominator of R is an even number. When the sum is odd, the numerator and denominator of R must be doubled in order to get the simplest structure. This is apparent when equation 8-2 is rewritten as $2N_t$ = M + 3P, in which N_t is a whole number so that M + 3P must be an even number. Since multiplying an odd number by three gives an odd number, and multiplying an even number by three gives an even number, the sum of the denominator and numerator of R must be even for the minimum number of phosphorus atoms in a structure of a given ratio, R, to be the same as the denominator of the ratio. The sole exception to this rule occurs for the ratio, R = 1/1 where the formula is incapable of distinguishing between one linkage and two half-linkages. At R = 1, the predicted smallest structure is not made from PO_4 groups but is



in which the two P—O bonds act as half-linkages. At this composition, the smallest structure is really



Equation 8-2 is not particularly useful, but it may be employed to derive other equations which are.

Since a half-linkage is attributable to each cation (or organic radical) in a phosphate structure, it is seen that, if a half-linkage is subtracted for each cation in equation 8-2, the following results for the number of P—O—P linkages, N_p in a phosphate structure:

$$N_p = (3P - M)/2 \tag{8-3}$$

For compositions for which R is equal to or greater than unity, it is not necessary to employ branching points in building phosphate structures. However, in the ultraphosphate region, where R is less than 1, branching points must be used. It is convenient to differentiate these necessary

branching points, and we can do this by singling out one of the P—O—P linkages at a branching point and refer to it as a linkage in excess of the ones needed at the metaphosphate composition. These excess linkages, N_x, may be calculated by the following equation:

$$N_x = (\mathrm{P} - \mathrm{M})/2 \qquad \text{for P} > \mathrm{M} \tag{8-4}$$

The number of oxygen atoms in a phosphate structure can be computed from the following equation based on stoichiometry:

$$\mathrm{O} = \mathrm{M}/2 + 5\mathrm{P}/2 \tag{8-5}$$

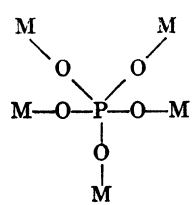
We are now able to use equations 8-2–8-5 as existence theorems to compute the smallest possible number of atoms in a phosphate structure corresponding to a given R, and examples of such calculations are shown in Table 8-6. For some values of R, single phosphate structures cannot be found. An example is $R = 7/3$. To determine quickly whether or not a single phosphate structure exists for a given R, the following inequality was developed:

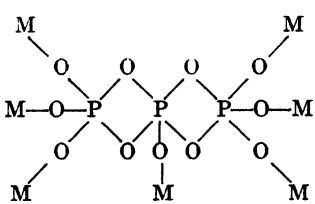
$$\mathrm{P} > \mathrm{N}_p + 1 \tag{8-6}$$

When P is greater than $N_p + 1$, at least two phosphate structures are required to satisfy the ratio R, except for $R = 3$. Naturally, for any values of P and N_p when $R < 3$, there can be a mixture of several structures Inequality 8-6 merely tells when there must be a mixture.

An example will best explain the use of inequality 8-6. Consider M/P = 7/3; equation 8-2 predicts $N_t = 8$, equation 8-3 predicts $N_p = 1$, equation 8-5 predicts O = 11, and by inequality 8-6, $3 > 1 + 1$. Therefore, two structures must exist, and it is seen that a mixture of $Na_4P_2O_7$ and Na_3PO_4 fulfills all requirements.

It is interesting to note that a solution of equations 8-3 and 8-5 in terms of $\mathrm{P} = N_p + 2$, a condition which violates inequality 8-6, leads to the formula: $\mathrm{M}_{n+4}\mathrm{P}_n\mathrm{O}_{3n+2}$. This formula corresponds to a nontetrahedral series of phosphates, a "pentavalent" phosphate series according to early authors, as is shown by the following monomer and trimer of the series:





For $\mathrm{P} = N_p + 3$, $N_p + 4$, etc., there are more M atoms than oxygen atoms for the lower members of the series. This means that single structures

TABLE 8-6
Smallest Possible[a] Number of Atoms in a Given M_2O/P_2O_5 Composition

$R =$ M_2O/P_2O_5	Minimum values of M	P	O	Corresponding values of N_t	N_p	N_x	Minimum number of separate structures	Probable structures
5	5	1	5	4	—		2	$M_2O + M_3PO_4$
3	3	1	4	3	0	—	1	M_3PO_4
5/2	10	4	15	11	1		3	$M_4P_2O_7 + 2\ M_3PO_4$
2	4	2	7	5	1		1	$M_4P_2O_7$
9/5	9	5	17	12	3		2	$M_5P_3O_{10} + M_4P_2O_7$
7/5	7	5	16	11	4		1	$M_7P_5O_{16}$
6/5	12	10	31	21	9		1	$M_{12}P_{10}O_{31}$
1	1	1	2 + 2 (1/2)	1 + 2 (1/2)	2 (1/2)	0		$[(MPO_3)_2]$
2/3	4	6	17	11	7	1	1	$(M_2P_3O_8)_2O$ (see Chapt. 12)
1/2	2	4	11	7	5	1	1	See Table 8-5 & Chapt. 12
1/3	1	3	8	5	1	1	1	See Table 8-5 & Chapt. 12
0	0	2	5	3	3	1	1	P_2O_5 (see Table 8-2)
Polyphosphate $2 > (n+2)/n > 1$	$n+2$	n	$3n+1$	$2n+1$	$n+1$	—	1	$M_{n+2}P_nO_{3n+1}$
Metaphosphate $n/n = 1$	n	n	$3n$	$2n$	n	0	1	$M_nP_nO_{3n}$
Phosphorus pentoxide $0/n = 0$	0	n	$5n/2$	$3n/2$	$3n/2$	$n/2$	1	$(P_2O_5)_{n/2}$

[a] This includes highly strained structures and those showing steric hindrance, all structures being made up from interlinked PO_4 groups.

for these hypothetical lower members would have to include M—P bonds, which should not be found in a phosphate.

Formula for Chain Phosphates[9]

Now we shall derive structure formulas for the various types of phosphates. In chain phosphates, there must be one more phosphorus atom

than the number of P—O—P linkages; hence, $N_p = P - 1$. By substituting $P - 1$ for N_p in equation 8-3, we find

$$N_p = (3P - M)/2 = P - 1 \tag{8-7}$$

or

$$M = P + 2$$

From equation 8-5

$$O = M/2 + 5P/2 = (P + 2)/2 + 5P/2 + 3P + 1$$

Hence, if the number of phosphorus atoms is n, the over-all formula must be

$$M_{n+2}P_nO_{3n+1} \tag{8-8}$$

The rule that there is one more phosphorus atom than the number of P—O—P linkages applies to all chain phosphates, independent of the amount of branching, as long as the branches do not come together so as to form rings. Formula 8-8 then applies to the homologous series of phosphates consisting of either straight or branched chains. When $n = 0$, the formula vanishes; but when $n = 1$, the formula converts to that for the orthophosphate, M_3PO_4. For $n = 2$, we obtain the pyrophosphate formula, $M_4P_2O_7$; and, for $n = 3$, the tripolyphosphate formula, $M_5P_3O_{10}$, etc. In the limiting case of very high degrees of polymerization, the formula for chain phosphates, which is identical to the classical formula for polyphosphates, gives a highly polymerized metaphosphate:

$$\lim_{n\to\infty} M_{n+2}P_nO_{3n+1} = (MPO_3)_n \tag{8-9}$$

It is instructive to write formula 8-8 in the old double-oxide notation: $(n + 2)M_2O \cdot nP_2O_5$. This means that $R = (n + 2)/n$ for any chain phosphate. Since a straight chain is made out of a number of middle groups (for which there is one M per P) between two end groups (for which there are two M's per P), it is seen that R must equal $(n + 2)/n$ for such a structure. When a branch is put on such a straight chain, we add one branching point (which has no M for its P) plus one end group and any number of middle groups. Since the branching point just balances out the added end group, the branch to the chain is equivalent with respect to R to simply making the chain longer so that, for the over-all structure, R still equals $(n + 2)/n$.

Formula for Ring Phosphates[9]

In a simple ring, the number of phosphorus atoms equals the number of P—O—P linkages; and this is also true if any number of straight or branched chains of any size are attached to the ring as long as the chains do not connect to each other to form fused rings. In this case, N_p = P and substitution of this value in equation 8-3 and then equation 8-5, as was done for the chain compounds, gives the formula for the ring phosphates, $M_nP_nO_{3n}$, which shows that such structures can only exist at the metaphosphate composition, $R = n/n = 1$.

If the metaphosphate formula is written in the old double-oxide notation, it becomes $nM_2O \cdot nP_2O_5$. Since for middle groups there is one M per P, any structure made completely out of middle groups will fit the metaphosphate formula. Furthermore, if we simultaneously add a branching point and an end group to the collection of middle groups making up the structure, the requirements for R = n/n = 1 are still fulfilled. This is another way of saying that simple rings, and rings with either straight or branched chains leading from them, must have the formula $M_nP_nO_{3n}$. A chain connecting two rings violates this formula, since two branching points are incorporated into the structure without the compensating effect of two end groups. Such a substance must have a composition lying in the ultraphosphate region.

General Formula for All Phosphates[9]

For the ultraphosphate system, no simple chemical formula exists that is completely comparable to the polyphosphate and metaphosphate formulas. A general chemical formula may be derived, however, that incorporates the M_2O/P_2O_5 ratio, R, as one of the parameters.

If P + N_x is substituted for N_p in equation 8-3 and the oxygen contained in the system is calculated from equation 8-5, the following formula may be derived:

$$M_{n-2N_x}P_nO_{3n-N_x} \tag{8-10}$$

but this formula is not in a convenient form. It is easily seen that

$$M_2O/P_2O_5 = M/P = R$$

and

$$M = PR$$

Also, P in the foregoing equation is equal to n in the general formula, therefore

$$M = nR \tag{8-11}$$

Thus equating nR to the subscript of M in the general formula

$$nR = n - 2N_x$$

or

$$N_x = (n - nR)/2$$

and, substituting this value for N_x in the subscript of O in the general equation, the oxygen of the phosphate may also be expressed as a function of R Therefore,

$$M_{nR}P_nO_{3n-(n-nR)/2}$$

or

$$M_{nR}P_nO_{n(5+R)/2} \tag{8-12}$$

When $R = 0$, this expression reduces to $P_nO_{5n/2}$ or $(P_2O_5)_{n/2}$, the formula for all of the polymers of phosphorus pentoxide. When $R < 1$, the formula describes the ultraphosphates. When $R = 1$, the general formula reduces to $M_nP_nO_{3n}$, which corresponds to the formula for metaphosphate rings. When $R = (n + 2)/n$, the formula becomes that of the polyphosphates, $M_{n+2}P_nO_{3n+1}$. Naturally, when $R = 3$ and $n = 1$, the formula reduces to the orthophosphate, M_3PO_4, as does the polyphosphate formula also.

Application of General Formula to Ultraphosphates[9]

The chemical formula shown above as equation 8-12 is particularly useful because the empirical formulas for the phosphate or phosphate mixture corresponding to a given M_2O/P_2O_5 ratio in the ultraphosphate range may be easily obtained. It is also seen that not only the total phosphorus present in the molecule is responsible for the chemical formula of the compound, but the M_2O/P_2O_5 ratio is also a parameter when the phosphate is cross-linked.

In any molecular species, the constituent atoms must be present in whole-number amounts. This means that in the formula, $M_{nR}P_nO_{(5+R)n/2}$, the subscripts—nR, n, and $(5 + R)n/2$—must be whole numbers. In order to find the lowest value for n, the degree of polymerization, in an ultraphosphate having a given value of R, the terms nR and $(5 + R)n/2$ must be

made integer Now it is not so difficult in most cases to make nR an integer as it is to make $(5 + R)n/2$ an integer Therefore we can let

$$n(5 + R) = j \qquad \text{where } j = 10, 12, 14, 16, 18, \ldots, \infty \qquad (8\text{-}13)$$

and get n_{min} for the smallest possible value of j, which is j_{min} In other words, when n times $5 + R$ is the smallest possible even whole number, the resulting value of n gives the minimum number of phosphorus atoms needed in a single ultraphosphate structure having the given value of R. It is immediately obvious that the smallest values of n in the ultraphosphate composition range occur at R = 0, $^1/_3$, $^1/_2$, and 1 For $R = 0$, we find that $n = 2$ corresponding to the formula P_2O_5. For $R = {}^1/_3$, we find that $n = 3$, and the resulting formula is MP_3O_8; and for $R = {}^1/_2$, we find that $n = 4$, and the resulting formula is $M_2P_4O_{11}$ For $R = 1$, we find that $n = 2$, and the resulting formula is $(MPO_3)_2$, the dimetaphosphate.

Changing the value of R very slightly from the rational fractions at which low numbers are found for n_{min} gives extremely large values for n_{min} Thus, if R is increased from $^1/_2$ to 0 5001, n_{min} jumps from 4 to 2000. A similar decrease in R also gives large values of n_{min} This means that low molecular weight ultraphosphates will only occur at values for R which are rational fractions. Crystalline ultraphosphates will most probably contain either these low molecular weight molecule-ions or extremely high molecular weight molecule-ions, such as would appear in sheet structures. In the case of the crystals having low molecular weight molecule-ions, values of R intermediate between the rational fractions would surely correspond to mixtures of simple structures for each of which the numerator and denominator of R would be small whole numbers.

By returning to the meaning of $R = M_2O/P_2O_5$ and writing the formula for the ultraphosphate in the Berzelius notation as $[R(M_2O)](P_2O_5)$, we see that for proper fractions such as $^3/_7$, $^5/_9$, $^1/_3$, etc., the value of $n_{min.}$ will always be exactly once or twice the denominator of R. When the sum of the numerator plus denominator of R is even, $n_{min.}$ equals the denominator of R. When the numerator plus denominator is odd, $n_{min.}$ equals twice the denominator. Thus, for example

$$(^3/_7)M_2O \cdot (1)P_2O_5 \text{ gives } 3\ M_2O \cdot 7\ P_2O_5 = M_6P_{14}O_{38}$$

$$\therefore n_{min} = 7 \text{ corresponding to } M_3P_7O_{19}$$

$$^2/_5\ M_2O \cdot (1)P_2O_5 \text{ gives } 2\ M_2O \cdot 5\ P_2O_5 = M_4P_{10}O_{27}$$

$$\therefore n_{min.} = 10 \text{ corresponding to the above formula}$$

Instability of Branching Points

In 1950, Van Wazer and Holst said that "In any environment in which reactions involving the degradation of condensed phosphates are possible, it is to be expected that assemblies in which three of the four oxygens of a PO_4 tetrahedron are shared with other PO_4 tetrahedra will be exceedingly unstable and will degrade much more rapidly as compared to those in which one or two oxygens are shared. Such an environment is found, for example, in aqueous solution."[12] This conclusion, which is called[13] the Antibranching Rule, was originally based on x-ray and pH titration data. These and other demonstrations of the rule will be reviewed below:

1. The concept that branching points are relatively unstable originally came in great part from a review of x-ray data.[12,13] In the orthophosphates in which the PO_4 group is not bound (as with hydrogen bonds) to other atoms or groups in the crystal, all four P-O distances are equal and correspond to 0.3–0.4 π-bond per σ-bond. In an end PO_4 group, the three connections to isolated oxygen atoms show a little more π-character, 0.5–0.6 π-bond per σ-bond. In a middle PO_4 group, the two connections to isolated oxygen atoms show even more π-character, whereas the two connections to the bridging oxygens exhibit less π-character (0.1–0.3 π-bonds per σ-bond) than the P-O connections in the orthophosphate group. Finally, in P_4O_{10}, the branching-point PO_4 groups show an extreme unbalance in the distribution of π-character among the four P-O connections. In this case, the one connection to the single isolated oxygen atom is alleged to have 1.4–1.9 π-bonds per σ-bond, whereas the three connections to bridging oxygens exhibit practically no π-character (0.1–0.2 π-bond per σ-bond). These results indicate that the branching-point PO_4 group totally lacks the resonance which stabilizes the orthophosphate PO_4 group. Unbalance of the π-character is observed in end and middle groups, but the greatest increase in unbalance appears to be observed when going from a middle group to a branching point—hence the Antibranching Rule. Interionic effects, such as hydrogen bonding, in a phosphate crystal tend to obscure the changes in π-bond distribution when going from isolated to end to middle to branching PO_4 groups. Thus, more than two different P-O atom-center distances are found in the $P_4O_{12}^{4-}$ ring of ammonium tetrametaphosphate

[12] J. R. Van Wazer and K. A. Holst, *J. Am. Chem. Soc.*, **72**, 639 (1950).
[13] J. R. Van Wazer, *J Am. Chem. Soc.*, **78**, 5709 (1956).

2. pH titration[12] of more than 100 different phosphates shows a strong acid function for each phosphorus atom in any of the compositions studied. Since hydrogen and phosphorus exhibit approximately the same electronegativity (see Table 2-2), the effect of the covalent bonding of hydrogen atoms on a PO_4 group should be quite similar to the effect of sharing of oxygen atoms with other PO_4 tetrahedra. Thus, in aqueous solution, only those phosphates should be detectable in which the number of σ-bonds connecting the oxygens of a single PO_4 group to either another phosphorus atom or to hydrogen is less than three. According to Van Wazer and Holst,[12] one would expect that in a PO_4 group in which three of the oxygens were covalently bonded to atoms other than the central phosphorus atom, one of the three bonds would break upon dissolution in water. Naturally, if one of these bonds were an O—H bond, the hydrogen should immediately ionize in water to produce a completely dissociated proton, in order to avoid the complicated hydrolysis process involved in breaking a P—O—P linkage. In other words, in aqueous solutions of pure phosphoric acids, there should be one strongly ionized hydrogen for each phosphorus atom, as has been found.

3. At present, the most convincing proof that degradation of branching points occurs at an unconscionably high rate is found in recent studies[14,15] of the hydrolytic degradation of long chain phosphates which exhibit some crosslinking. When branching points appear in either crystalline (Kurrol's salt) or amorphous (Graham's salt) long chain phosphates, it is found that the intrinsic viscosity of dilute aqueous solutions exhibits a rapid initial drop which can be attributed to scission of the crosslinks.[14] In the most careful study of this effect to date,[15] it was found that the rate constant for the hydrolytic scission of P—O—P linkages so as to change a branching point into a middle group is $8(\pm 4) \times 10^{-3}$ min.$^{-1}$ at 25°C. This scission is approximately a thousand-fold faster than the splitting of P—O—P linkages between two middles or a middle and an end group at the same temperature and neutral pH. Furthermore, the rate appeared to be independent of pH and concentration of added simple sodium salt—a phenomenal state of affairs when compared with the extreme variation with pH found for the hydrolytic degradation of "normal" P—O—P linkages.

[14] U. P. Strauss, E. H. Smith, and P. L. Wineman, *J. Am. Chem. Soc.*, **75**, 3935 (1953), and R. Pfanstiel and R. K. Iler, *J. Am. Chem. Soc.*, **74**, 6062 (1952).

[15] U. P. Strauss and T. L. Treitler, *J. Am. Chem. Soc.*, **77**, 1473 (1955); *ibid.*, **78**, 3553 (1956).

4. Unfortunately, there is a paucity of thermodynamic data on the condensed phosphates. However, the following heats of reactions (from Appendix C) are in accord with the idea that branching points are particularly unstable thermodynamically.

$$P_4O_{10}(c) + 6\,H_2O(l) \xrightarrow{\Delta H \pm 56.2\text{ kcal.}} 4\,(HPO_3)_r(c) + 4\,H_2O(l) \xrightarrow{\Delta H = 26.6\text{ kcal}}$$
$$2\,H_4P_2O_7(c) + 2\,H_2O(l) \xrightarrow{\Delta H = 12.2\text{ kcal.}} 4\,H_3PO_4(c) \quad (8\text{-}14)$$

In the first step of this sequence of reactions, all of the branching points are converted to middle groups, and an amount of heat equal to 28.1 kcal./mole of P—O bonds being broken was liberated. In going from middle to end groups, 13.3 kcal./mole of P—O bonds being broken is obtained, and in going from end groups to orthophosphate there is 6.1 kcal./mole of split P—O bonds. The 13.3 kcal. corresponds to the enthalpy of a "high-energy" bond of the biochemists,[16] whereas the 6.1 kcal. is quite low, corresponding to a value usually associated with a "low-energy" bond, although the pyrophosphate ion degrades completely to orthophosphate in dilute aqueous solution (and hence is a high-energy phosphate by definition). The bond to the branching point seems to represent a "super high- energy" bond.

5. A number of miscellaneous chemical data appear to bear out the contention that branching points are unstable with respect to the other types of PO_4 groups. Thus, sodium phosphate melts[17] in the ultraphosphate range of composition will absorb sufficient water at temperatures in the range of 300–500°C. to bring the composition to that of the metaphosphate [$R = (Na_2O + H_2O)/P_2O_5 = 1$]. The reverse of this is the well-known idea found among phosphate chemists that condensation reactions in which water is removed at high temperatures from orthophosphates do not proceed much beyond the metaphosphate composition. A glaring exception to this rule-of-thumb is found, however, in azeotropic phosphoric acid. This acid contains[18] 92.1% P_2O_5 when boiled under a pressure of 753 mm. of Hg at 869°C. As the azeotropic acid consists of only H_2O and P_2O_5, R for this compound equals 0.67, and this corresponds to an ultraphosphate in which one-third of the PO_4 groups are branching points. Since vapor density measurements[18] indicate that the vaporized phosphoric acids dis-

[16] For example, P. Oesper, *Phosphorus Metabolism*, eds. W. D. McElroy and B. Glass, Johns Hopkins Press, Baltimore, Md., 1951, Vol. I, pp. 521–36; N. O. Kaplan, *The Enzymes*, ed. by J. B. Sumner and K. Myrback, Academic Press, New York, 1951, Vol. II, Part 1, pp. 55–113.

[17] Private communication from E. J. Griffith of the Monsanto Chemical Company.

[18] E. H. Brown and C. D. Whitt, *Ind. Eng. Chem.*, **44**, 615 (1952).

sociate into H_2O and P_4O_{10} at temperatures near 1000°C., the presence of branching points in the azeotrope is not too surprising. Presumably, at the elevated temperatures involved, the postulated energy difference between branched and unbranched structures has disappeared.

An example of a related type of reaction which does fit the rule is the reaction between phosphorus pentoxide and salt. This reaction proceeds[19] according to the following classical equation but will not go farther than the metaphosphate composition

$$2\ P_2O_5 + 3\ NaCl \xrightarrow{\Delta} 3\ NaPO_3 + POCl_3\uparrow \qquad (8\text{-}15)$$

When a dry mixture of salt and sodium metaphosphate are melted together, there is no reaction[20] even after many hours in spite of the fact that equations such as the following can be written

$$3\ NaPO_3 + 3\ NaCl \dashrightarrow 2\ Na_3PO_4 + POCl_3\uparrow \qquad (8\text{-}16)$$

Although a number of additional examples can be quoted, we shall present the controlled hydrolysis of the P_4O_{10} molecule as the last chemical evidence given here for the relative instability of branching points. As shown on page 693, the α-form of phosphorus pentoxide hydrolyzes to give a large yield of the simple ring compound, tetrametaphosphoric acid, plus a small amount of low molecular weight degradation products, such as ortho- and pyrophosphate. This rapid hydrolysis of P_4O_{10} is, of necessity, the hydrolysis of crosslinkages, and the formation of a preponderant amount of tetrametaphosphate is evidence that crosslinked and branched phosphates are less stable than structures in which only end groups and middle groups appear.

Although none of the information reported above is definitive, it may be concluded that the Antibranching Rule of Van Wazer and Holst is correct to better than the first approximation for ionic, and perhaps for un-ionized, phosphates. This means that branched structures will be present in only inappreciable amounts in solid ionized compositions made at temperatures sufficiently high so that reorganization can take place, when the M_2O/P_2O_5 ratio is greater than unity. Furthermore, there will be only a very small and quickly vanishing proportion of the total number of PO_4 groups pres-

[19] C. R. McCullough and F. C Jelen, unpublished data, Monsanto Chemical Company (1935); also see G. Tarbutton, E. Egan, and S. Frary, *J. Am. Chem. Soc.*, **63**, 1782 (1941); and H. A. Curtis, R. L. Copson, and A. J. Abrams, *Chem. & Met. Eng.*, **44**, No. 3, 140 (1937).

[20] C. F. Callis and J. S. Metcalf, unpublished data, Monsanto Chemical Company.

ent as branching points in aqueous *solutions* of any phosphate anion unless the branching points are artfully protected by steric hindrance

DIFFERENTIAL ANALYSIS OF PHOSPHATE MIXTURES

Ever since it was discovered that there were a number of different phosphates, chemists have been attempting to develop analytical procedures for differentiating and quantitatively determining the individual constituents present in various phosphate mixtures. The literature on this subject is voluminous. Until the last few years, all of the work on separating phosphate mixtures was based on wet-chemical methods. These methods include precipitation with barium, silver, manganese, luteocobaltic chloride, and a number of organic cations.[21] Albumen has also been described for nearly a century and a half[1] as a selective precipitant for the variety of "metaphosphoric acid" which we now know consists of long chain phosphates.

The more recent modifications of these classical, analytical procedures which are still somewhat popular at the present time in the United States are the techniques of Jones[22] and Bell. In the Jones' procedure, the long chain phosphates, which he calls "hexametaphosphate" are precipitated in acid solution with barium, then pyrophosphate is precipitated from a separate aliquot at a pH of 4.1 as the manganous salt. Orthophosphate is separately determined with ammonium molybdate. The trimetaphosphate (and, indeed, the other well-known ring phosphate, the tetrametaphosphate) is determined as the phosphate which does not precipitate with barium in an alkaline solution. The so-called "polyphosphates," which are chain phosphates of intermediate length, are then obtained by difference. The Bell procedure uses a zinc titration for the determination of the tripolyphosphate.

Unfortunately, even the most careful work in the development of wet-chemical procedures for the differential analysis of phosphate mixtures has not led to success when applied to a large variety of such mixtures.[23] Fur-

[21] As is the case with all of the early literature on phosphates, the terminology used in describing the various phosphates in the analytical literature is most confusing. A great deal of this early literature is written in terms of ortho-, pyro-, and metaphosphate, and the obvious qualitative difference between the long chain "metaphosphates" and the ring "metaphosphates" was often a source of puzzlement and confusion. An example of early work in this field is Braun, *Z. anal. Chem.*, **3**, 468 (1864).

[22] L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942); R. N. Bell *et al.*, *Anal Chem.*, **19**, 97 (1947), and *ibid.*, **24**, 1997 (1952).

[23] For an example of a recent wet-chemical procedure which was very carefully tested, see H. W. McCune and G. J. Arquette, *Anal Chem.*, **27**, 401 (1955).

thermore, for long chain phosphates, the various precipitation methods turn out to be no more than a rough solubility fractionation into overlapping groups of phosphates, each group of which covers a relatively broad range of molecular weights. A recent paper by Dewald[24] has pointed out the unsatisfactory character of several of the procedures for quantitatively determining mixtures of pyro- and tripolyphosphate.

Although traditional wet-chemical procedures are not very satisfactory for the condensed phosphates, orthophosphate can be determined to moderate precision in the presence of the condensed phosphates by either of two general techniques. In one of these techniques, the third hydrogen of the orthophosphate is released for titration by use of a strong precipitating agent. This technique was first developed by Gerber and Miles,[25] who employed silver as the precipitating agent. Although ions other than silver will also release the third hydrogen of the orthophosphate, a recent study indicated that silver is especially good for this purpose.[26] The other general technique is based on the fact that only the ortho form of the phosphates gives a heteropoly acid with molybdate. Since the phosphomolybdate precipitation is carried out in highly acidic solution, it is necessary to work fast and keep the solution cold in order to avoid hydrolysis of the condensed phosphates.[27] A number of modifications of the phosphomolybdate procedure are popular. Thus, the precipitate may be weighed, may be dissolved and back titrated, or extracted with a solvent such as ethyl acetate. The yellow phosphomolybdate precipitate may also be reduced to a blue compound which can be detected in trace amounts by colorimetric procedures. For a general review of the analytical chemistry of phosphorus, see the contribution of Klement[28] to *Handbook der Analytischen Chemie*.

During the last several years, the application of chromatographic techniques to differential analysis of phosphate mixtures has proven most successful, and it is believed that, exclusive of the determination of orthophosphate in phosphate mixtures, chromatographic techniques will completely supplant the wet-chemical procedures, except, perhaps, for some routine control work. By use of paper chromatography, as introduced by

[24] W. Dewald, *Fette u. Seifen*, **56**, 105 (1954).

[25] A. B. Gerber and F. T. Miles, *Ind. Eng. Chem., Anal. Ed.*, **13**, 406 (1941).

[26] J. R. Van Wazer, E. J. Griffith, and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954). E. J. Griffith, *ibid.*, **28**, 525 (1956).

[27] E. Karl-Kroupa, J. R. Van Wazer, and C. H. Russell, *Scott's Standard Methods of Chemical Analysis*, ed. N. H. Furman, 6th ed., D. Van Nostrand Co., New York, in preparation.

[28] R. Klement, *Handbook der Analytischen Chemie*, eds. W. Fresenius and G. Jander, Springer, Berlin, 1953, Sect. 3, Vol. Vaβ, pp. 305–22. Also see ref. 27.

Ebel[29] and Westman,[30] members of the family of chain phosphates as high as the dodecaphosphate have been separately determined as have the a number of ring phosphates.[31] Furthermore, two-dimensional chromatography can be used to distinguish unequivocably between the family of ring and the family of chain phosphates. Complete data on the two-dimensional chromatography[29,31] are given in Figure 11-7 (p. 703). The paper chromatographic technique is capable of high precision[31] and appears to be fundamentally sound Work on separation of phosphate mixtures by paper electrophoresis also offers interesting new possibilities.[32] In the regular moving-solvent technique of paper chromatography, the long chain phosphates do not leave the origin; however, in paper electrophoresis even the highest molecular weight chain phosphates are found to move. The problem here is that the long chains move primarily in the direction of their length, with the charge on each PO_4 group acting as the driving force. This means that, although the long chain phosphates move from the origin, long and short chains tend to move together in a body during paper electrophoresis. Paper chromatography has also been very successful in separation of the various esters of both orthophosphate and condensed phosphates.[33] These latter techniques are of great importance to biochemistry, where the phosphate esters play an important role (see Chapts. 21 and 22).

Anion exchange resins are also suitable in separating mixtures of phosphates.[34] In this technique, the phosphate is put on the top of a column and is then selectively eluted. Although ion exchange chromatography has not yet been successful in separating phosphates higher than the dodecapolyphosphate,[35] it offers great hope for the future in making separa-

[29] J. P. Ebel, *Compt. rend.*, **233**, 415 (1951); *ibid*, **234**, 621 (1952); *Bull. soc. chim. France*, **20**, 991 (1953).

[30] A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951); A. E. R. Westman, A. E. Scott, and J. Pedley, *Chemistry in Can.*, **4**, 189 (1952); and J. Crowther, *Anal. Chem.*, **26**, 1383 (1954).

[31] E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956); J. R. Van Wazer and E. Karl-Kroupa, *J. Am. Chem. Soc.*, **78**, 1772 (1956).

[32] B. Sansoni and R. Klement, *Angew. Chem.*, **16**, 442 (1953); and *ibid.*, **19**, 598 (1954).

[33] C. S. Hanes and F. A. Isherwood, *Nature*, **164**, 1107 (1949); L. V. Eggleston and R. Hems, *Biochem. J.*, **52**, 156 (1952); A. Fleckenstein and E. Gerlach, *Arch. exp. Pathol. Pharmakol.*, in press; and *Naturwissenschaften*, **40**, 162 (1953).

[34] J. Beukenkamp, W. Rieman, and S. Lindenbaum, *Anal. Chem.*, **26**, 505 (1954). S. Lindenbaum, T. V. Peters, and W. Rieman, *Anal. Chim. Acta*, **11**, 530 (1954); J. A. Grande and J. Beukenkamp, *Anal. Chem.*, **28**, 1497 (1956); M. Matsuhashi, *J. Biochem.*, **44**, 65 (1957); H. J. Weiser, Jr., *J. Am. Oil Chemists' Soc.*, **34**, 124 (1957).

[35] J. H. Payne, unpublished results of Monsanto Chemical Company.

tions up to extremely high molecular weights, since it is possible to vary not only the resin itself but the eluting agent. Presumably, the separation of the long chain phosphates will be effected by the use of very powerful eluting agents on resins which have only a mild anion-binding capacity.

Although the chromatographic procedures offer some promise for separation of very long chain phosphates, they have not yet been developed to the point where they can do this job. There is, however, a good technique for making such separations. This is the method of solubility fractionation, such as is used in studying organic high polymers.[36] By adding water-soluble organic compounds (such as acetone or alcohol) to a mixture of high molecular weight polyphosphates,[37] individual fractions may be obtained which exhibit successively lower average molecular weights, as determined by any of the techniques of polymer physics. Simple salts, such as sodium chloride, can be used instead of organic materials to effect the precipitation of the phosphate. In this case, however, it is difficult to remove the lower molecular weight materials from solution. The barium precipitation technique of the type used by Jones can also be developed[38] into a type of solubility fractionation either by increasing the pH stepwise or adding incremental amounts of the barium salt.

Solubility fractionation with acetone or similar materials has one great advantage, in that the various fractions are not contaminated with salts other than phosphates and can easily be handled without much trouble in further chemical operations. Solubility fractionation can be carried out on a relatively large scale, so that kilogram fractions are obtained.

One of the most useful tools in the analysis of phosphate mixtures is pH titration. As has been shown,[12] there is one titratable strong acid hydrogen for each phosphorus atom and a titratable weak acid corresponding only to terminal or end-group phosphorus atoms. Thus, titration of any soluble phosphate between the end points near pH 4.5 and 9 gives the number of PO_4 end groups. Since in ortho- and pyrophosphates no middle groups are to be found, this same titration after hydrolysis of the more condensed forms gives the total number of phosphorus atoms.[26] When only chain phosphates are present, the number-average number, $\bar{n}$, of phosphorus atoms per chain is given by:

$$\bar{n} = 2(\text{total P})/\text{end-group P} \tag{8-17}$$

[36] L. H. Cragg and H. Hammerschlag, *Chem. Revs.*, **39**, 79 (1946).

[37] J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 647 (1950).

[38] For a beginning along this line, see W. Dewald and H. Schmidt, *Z. anorg. u. allgem Chem.*, **272**, 253 (1953); also unpublished data of Monsanto Chemical Company.

In the presence of orthophosphate or rings (metaphosphates), this equation must be corrected as follows:

$$\bar{n} = \frac{2(\text{total P} - \text{orthophosphate P} - \text{ring P})}{(\text{end-group P} - \text{orthosphosphate P})} \tag{8-18}$$

The average number of phosphorus atoms per chain can be apportioned among the various chains, since:

$$\frac{1}{\bar{n}} = \sum_i \frac{x_i}{n_i} \quad \text{and} \quad \sum_i x_i = 1 \tag{8-19}$$

where x_i is the fraction of the total phosphorus atoms in the ith chain, and n_i is the number of phosphorus atoms in the ith chain. For only two chain phosphates this equation reduces to the following form:

$$x_A = \frac{(n_A n_B/\bar{n}) - n_A}{n_B - n_A} \tag{8-20}$$

where $n_B > n_A$ This means that mixtures of two chain phosphates plus the monomer —mixtures such as ortho-, pyro-, and tripolyphosphate—can be unequivocably analyzed[26] in terms of the molecular species present.

It is interesting to note that by means of nuclear magnetic resonance, the relative amounts of orthophosphate, end groups, middle groups, and probably branching points can be determined with reasonably good accuracy.[10] This procedure is especially useful for concentrated samples which are present in liquid form.

In certain analytical procedures, radioactive phosphorus has been used as a tracer. In order to do this properly, it is important that the phosphorus does not exchange between the species to be differentiated. Fortunately, this is the case for the phosphates, which do not exchange[39] with other phosphorus compounds (phosphites, hypophosphites, etc.) in aqueous solution. Moreover, the various condensed phosphates do not exchange with each other nor do orthophosphate esters exchange with the orthophosphate ions. It is probably safe to conclude that, when radioactive phosphorus in a specific phosphate appears in another phosphorus-

[39] V. D. Ionin, A. F. Lukovnikov, M. B. Neĭman, and An. N. Nesmeyanov, *Doklady Akad. Nauk S.S.S.R.*, **67**, 463 (1949); J. N. Wilson, *J. Am. Chem. Soc.*, **60**, 2697 (1938); A. F. Lukovnikov, V. P. Medvedev, M. V. Neiman, An. N. Nesmeyanov, and I. S. Shaverdina, *Doklady Akad. Nauk S.S.S.R.*, **70**, 43 (1950); O. T. Quimby, A. J. Mabis, and H. W. Lampe, *Anal. Chem*, **26**, 661 (1954); D. E. Hull, *J. Am. Chem. Soc.*, **63**, 1269 (1941); D. R. H. Gourley, *Atomic Energy Commission Document AECU-1763*, May, 1952.

based compound, the second compound must have been formed from the particular phosphate which was radioactive originally.

COMPARISON OF CONDENSED PHOSPHATES WITH CONDENSED OXYACIDS OF OTHER ELEMENTS

A general property of the oxyacids and their salts is "anionic condensation."

The use of the word "acid" in such forms as "oxyacid," "polyacid," etc., in this discussion may present semantic difficulties to many inorganic chemists. Unfortunately, the alchemical notation of acids *vs* bases *vs* salts still persists in the chemical argot, even though for purposes of this discussion, the acid might better be considered as a hydrogen salt and the base as a salt of the hydroxide ion, where salts are defined as those chemical compounds which form anions plus cations in solution and often in their solids I have classed as salts of isopoly acids many substances for which the free acid is nonexistent I have also put into this class compounds which break down during the process of dissolution to give simpler anions than would be expected.

In this process the simple molecule-ions (often of the form XO_4^{n-}, where the X atom is tetrahedrally surrounded by the four oxygens) condense together by loss of water to give more complex structures. If a single acid anhydride (only one kind of X) is involved, the anions corresponding to the complex structures are called "isopoly" anions; but, if several acid anhydrides are involved, the complex anions are called "heteropoly" anions. Examples of isopoly acids and/or their salts are found in the condensed phosphates discussed above, the borates, aluminates, silicates, arsenates, sulfates, and the anions based on the related subgroup metals such as vanadium, chromium, and molybdenum. It appears that highly complex anions can be built up from the simple anions corresponding to the oxyacids of a large number of elements. The general method of carrying out the dehydration which converts a simple oxyacid to a polyacid is by heating acid salts or mixtures of acid and salt to elevated temperatures at which the water of composition is vaporized.

Heteropoly acids and/or their salts can be made from a large combination of the simple anions of the various oxyacids; but the heteropoly acids which have been most frequently described in the literature are the complex oxyacids based on either tungsten, molybdenum, or vanadium plus one of the wide variety of other elements forming oxyacids. The phosphomolybdates, tungstates, and vanadates are described in Chapter 9 (pp. 559–569) as they are derivatives of orthophosphates, whereas the salts of the polyacids corresponding to mixed phosphate-arsenates, phosphate-sulfates, etc. are described in Chapters 10 and 12.

Because of insufficient data, it is difficult at the present time to compare properly the oxyacids of the various elements with respect to their ability to form condensed species (either the polyacids or their salts) and with respect to the stability of the condensed forms. There is one class of oxyacids, however, which seems to be reasonably well typified This class consists of those anions which build up or degrade in size as the pH is changed. In this type of system --exemplified by the chromates and molybdates-- there appears to be an equilibrium between the various sized anions even in relatively dilute aqueous solutions,[40] with the average size becoming greater as the pH is lowered. This behavior is believed to be typical of the oxyacids of the transition or subgroup elements.

The polysulfates (of which the pyro acid and its salts and the nitronium[41] salt of the tripoly acid have been crystallized) degrade very rapidly to the simple sulfate upon dissolution in water Furthermore, the polysulfates cannot be obtained from dilute solution. Although only the di- and trimembers of the homologous series of polysulfates have been isolated, Raman spectra and cryoscopic data[42] indicate that oleums (mixtures of H_2SO_4 and SO_3) contain tetra- and perhaps higher polysulfates.

The polyborates are similar to the polysulfates in that they decompose to the simple orthoborate in acid solution, and, indeed, light scattering and ultracentrifuge measurements, as well as other data, indicate that the borate ions present in solution (exhibiting various ratios of Na_2O to B_2O_3) contain only one boron atom.[43,44] However, potassium pentaborate, which has a known structure involving a polyborate anion, as well as other borates (such as borax) which may be the salts of polyacids, can be crystallized from the aqueous solutions which are thought to contain only the simple monoborate ions. The pentaborate crystals must be in equilibrium with an undetectably small amount of dissolved pentaborate ion, but it may at the same time be possible that the condensation to form the pentaborate anions occurs on the crystal surfaces. Of course, polyborates can be made by the

[40] For typical data on the molybdates, see I Lindquist, *Acta Chem. Scand.*, **5**, 568 (1951); G. Jander, K. F. Jahr, and W. Henkeshoven, *Z. anorg u allgem. Chem.*, **194**, 383 (1930); also see A R Middleton, *J Chem. Educ.*, **10**, 726 (1933); I. Lindquist, *Nova Acta Regiae Soc Sci Upsaliensis, IV*, **15**, No. 1 (1950) for general information

[41] D. M. Goddard, E. D Hughes, and C. K. Ingold, *J Chem Soc.*, **1950**, 2559.

[42] D. J. Millen, *J Chem. Soc.*, **1950**, 2589; R. J. Gillespie, *ibid.*, **1950**, 2516

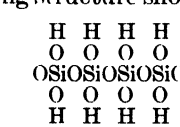
[43] A. W. Laubengayer and R. D. Rosenstein, *Preprint of papers for Symposium on Complex Ions and Polyelectrolytes*, American Chemical Society, Ithaca, N. Y., June 18–21, 1951, pp. XI–1–9.

[44] T. Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1952, pp. 308–11.

usual procedure of dehydration of acid salts. Sodium and potassium trimetaborates, as well as cobalt pyroborate, have been prepared by this technique.

The structures of the crystalline silicate minerals have been well established;[45] but the literature on the constitution of soluble and molten silicates is in a state of confusion.[46] All of the crystalline silicates exhibit anions based on SiO_4 tetrahedra—which appear as isolated groups ($R \equiv M_2O/SiO_2 = 2$), end groups ($R = 1.5$), middle groups ($R = 1.0$), three-way branching groups ($R = 0.5$), and four-way branching groups ($R = 0$) These building units are found to be assembled into rings, chains, cages, sheets, and crosslinked molecule-anions The crystalline silicates for which structures have been determined cannot be dissolved without destruction of the anions. The only soluble silicates are the alkali metal salts, of which the sodium compounds have been the best characterized A number of crystalline sodium silicates, which must exhibit anionic structures based on more than one silicon atom, have been described, and the series of soluble Na_2O–SiO_2 glasses, the "waterglasses," is well known. When the Na_2O/SiO_2 mole ratio is greater than about 0.5, the glasses are readily water soluble. For smaller ratios, steam must be used to obtain dissolution. The ratio of 0.33 is the approximate borderline between the clear sodium silicate solutions (high Na_2O) and the solutions in which colloidal particles containing hydrated SiO_2 occur.

The Antibranching Rule does not seem to apply to silicates, since the Si-O distances within an SiO_4 tetrahedron are equal to each other and do not change much from one structural unit to another In line with this, silicic acid is very weak[47] ($pK_1 \approx 10$ and other pK's > 12) Therefore, one would expect that a reorganizing system of this type would exhibit a mixture of all of the structure units plus the isolated SiO_4 group for a wide range of M_2O/SiO_2 ratios. Naturally, the oxygen atoms not connecting pairs of silicon atoms will be predominantly present as OH groups, so that a typical chain might have the following structure showing little charge.



[45] For example, G. W. Morey, *Encyclopedia of Chemical Technology*, eds. R. E. Kirk and D. F. Othmer, Interscience Publishers, Inc., 1954, Vol. 12, pp. 268–302.

[46] R. K. Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, 1955; also see W. Eitel, *The Physical Chemistry of the Silicates*, University of Chicago Press, Chicago, 1954.

[47] P. S. Roller and G. Ervin, *J. Am. Chem. Soc.*, **62**, 461 (1940).

Although very little structurally interpretable work has been carried out on silicate solutions, a careful study by light scattering,[48] after filtration to remove colloidal material (structures containing a number of branching points), shows that species of a size which is predictable by an extension of the random reorganization theory given in Chapter 12 are found. In view of the fact that addition of acid to any silicate solution causes condensation to the three-dimensional high polymer (hydrated silica) which precipitates out of solution, and since this precipitate, when fresh, can be redissolved by addition of alkali, it would appear that the silicates are in the same class as the isopoly vanadates, chromates, and molybdates.

A tentative classification of the oxyacids and their salts based on their degree of condensation in solution would, at the present time, divide these substances into two classes. The first class would consist of those materials which give a distribution of various sized anions in solution, with the distribution shifting toward larger structures as the pH is lowered. The second class would consist of those anions which degrade to the simplest structure—the first member of the homologous series—in solution. If the reported data on borates are reliable, it would seem that higher members of the homologous series can sometimes be crystallized from solutions in which the concentration of the higher members is essentially nil.

It appears that the "isopoly" phosphates are members of the second class of oxyacids defined above. However, many of the "heteropoly" structures in which the orthophosphate is condensed with anions of oxyacids based on elements other than phosphorus seem to be members of the first class. Examples of these "heteropoly" structures are found in the phosphomolybdates, phosphovanadates, etc., as well as in the derivatives of "mixed acid anhydrides" of organic phosphorus chemistry.

The concept of "high-energy" and "low-energy phosphate bonds" used by the biologists applies to the oxyacids discussed here. Since the term "energy" as used with respect to phosphate bonds is the free energy of hydrolysis, this means that the equilibrium between the unhydrolyzed material (the polyacid or its salt) and the hydrolyzed material (the ortho- or monoacid, as final product) is shifted far toward the first member of the homologous series in the case of the high-energy bonds, and that there is a measurable equilibrium in the case of the low-energy bonds. This "low energy" *vs.* "high energy" classification is thus seen to be practically identical to the classification made in the preceding paragraph between equilibrium (class 1) and degradation (class 2) kinds of polyacids and their salts.

[48] P. Debye and R. V. Nauman, *J. Phys. Colloid Chem.*, **55**, 1 (1951). The monomeric H_2SiO_3 discussed by these authors should be interpreted as $H_3SiO_4^-$ or $H_2SiO_4^{2-}$.

FORMATION OF CONDENSED PHOSPHATES

As described in Chapter 9, no condensed phosphates are ever found as minerals. However, the condensed phosphates play an important role in biology, where they are involved in energy transfer processes (see Chapt. 22). Both the formation and degradation of condensed phosphates in living systems appear to be enzymatically controlled. Presumably, the "high energy" phosphates are formed *in vivo* under conditions which are entirely different from the usual aqueous solutions for which M_2O/P_2O_5 (where M_2O includes *all* of the water) is far greater than three.[49]

In the laboratory, the various inorganic condensed phosphates are usually prepared by either the process of dehydration or the reverse of this process. Thus, various mixtures of acid orthophosphates can be either fully or partially dehydrated by heating at elevated temperatures, usually in the range of 300–1200°C. The general equations of such a dehydration reaction to form (*a*) the polyphosphates and (*b*) the ring metaphosphates are given below in terms of the sodium salts.

$$(a)\quad (n-2)\,NaH_2PO_4 + 2\,Na_2HPO_4 \longrightarrow Na_{n+2}P_nO_{3n+1} + (n-1)\,H_2O \qquad \text{for } n > 2 \qquad (8\text{-}21)$$

$$(b)\quad n\,NaH_2PO_4 \longrightarrow (NaPO_3)_n + n\,H_2O \qquad (8\text{-}22)$$

The ring and chain phosphates can also be made by the reverse procedure of adding such reagents as H_2O, NaOH, Na_2CO_3, NH_3, CaO, ZnO, etc., to phosphorus pentoxide or an ultraphosphate. Usually such reactions are very fast and exothermic, sometimes even explosively so.

The ultraphosphoric acids for which $R <$ about 0.8 must be made from either phosphorus pentoxide or another ultraphosphate exhibiting a smaller value of R. Usually ultraphosphates are prepared by adding phosphorus pentoxide to a material of the metaphosphate composition, although they can be produced by adding cationic reagents like H_2O, NaOH, and NH_3 to the phosphorus pentoxide.

It is common practice to make the esters and other organic derivatives of the condensed phosphates from phosphorus pentoxide.[50] This can be done by adding alcohols, acetone, ethers, etc., to the P_2O_5. A mixture of products is usually obtained from this reaction. A better controlled reaction is found in the classical method of synthesizing esters in which a silver

[49] The *in vitreo* condensation of sodium phosphates in dilute ($N/10$) solution has been reported rather recently by B. Sansoni, *Angew. Chem.*, **67**, 327 (1955). This report is believed to be false.

[50] See G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, Chapt. 12, pp. 333–54.

salt is reacted with a halide. The silver salts of condensed phosphates have been esterified by this technique, and P—O—P linkages have also been made by reacting a chlorophosphate with a silver salt of a phosphate. Thermal decomposition of halophosphates or of polyphosphate esters gives a mixture of polyphosphates. Controlled solvolysis of condensed phosphates or halophosphates has also been used to synthesize lower derivatives.

Most of the synthesis methods (and all of the purely inorganic ones) described in the above paragraphs involve sufficiently high temperatures and other factors so that reorganization can take place during synthesis. Therefore, one would not expect to make (1) monomeric P_2O_5, (2) structures containing dimetaphosphate rings, and (3) structures outside of the ultraphosphate region in which branching points are found since, as has been shown in the early part of this chapter, these structures are unstable with respect to other phosphates into which they might reorganize. Moreover, by the above-mentioned synthesis methods, the experimenter more or less has to take the structures which come from his experimental work, as he has not much control over the factors determining exactly which set of structures, or structure, results from the preparation of a phosphate having a given overall value of R. Such factors as the stabilizing energy of various crystal lattices, seeding, and relative velocities of various competitive crystallization processes play an important role. In vitreous and other amorphous compositions, the distribution of sizes and types of structures also seems to be a fixed quantity which cannot readily be altered by the experimentalist.

This means that in order to prepare phosphates which contain unstable arrangements of PO_4 groups as well as to make many specific compositions, it is desirable to develop techniques of placing given constituents at a specific point on a molecule or molecule-ion, such as is done in synthetic organic chemistry. Probably, techniques similar to those employed in preparing cyclopropane and cyclobutane can be used in synthesizing phosphate structures containing dimetaphosphate rings. Positional synthesis should also be quite applicable to low molecular weight branched-chain phosphates and complicated ring phosphates in which chains are attached to a single ring. Synthesis of these compounds represents a considerable challenge to the inorganic chemist.

An interesting approach to this type of synthesis consists of blocking off reactive sites[51] through esterification and then building up P—O—P linkages by reaction of chlorophosphates with silver phosphates. In this procedure,

[51] F. Lynen, *Ber.*, **73**, 367 (1940); A. R. Todd, *J. Chem. Soc.*, **1946**, 647; J. Baddiley and A. R. Todd, *ibid*, **1947**, 648; and J. Baddiley, A. M. Michelson, and A. R Todd, *Nature*, **161**, 761 (1948).

the benzyl group is used as the agent for blocking off unwanted acid functions on the phosphate. At the end of the reaction, the product is debenzylated by hydrogen, using palladium oxide as a catalyst.

Solvents for Phosphate Salts

At the present time only one good solvent is known for the alkali metal salts of the condensed phosphates, and this is water. Dioxane, liquid ammonia, anhydrous formic acid, dimethylformamide, various alcohols, glycols, glycerine, and other highly polar solvents have been tried and found to be unable to dissolve more than trace amounts of the sodium and ammonium salts of the condensed phosphates. The condensed phosphoric acids can be dissolved in a number of organic solvents, but it is believed that reaction usually takes place. This is probably also true for the ultraphosphates for which R is small, since phosphorus pentoxide reacts with ethers, alcohols, ketones, and other polar organic compounds, even at room temperatures.

The condensed phosphates of all metals except the alkali metals are usually quite insoluble, although the ring phosphates generally give salts that are considerably more soluble than are those of the chain phosphates.

HYDROLYTIC SCISSION OF P—O—P LINKAGES IN CHAINS AND RINGS

The condensed phosphates, as previously discussed, belong to the class of polyacids and their salts which hydrolyze to the uncondensed form in aqueous solutions. However, the chain and ring phosphates appear to be unique with respect to their extremely slow rate of hydrolysis. Instead of hydrolyzing about as fast as dissolution takes place, the half-life of these P—O—P linkages with respect to hydrolysis at neutral pH and room temperature is of the order of magnitude of years. This is the main reason why so much more is known about the condensed phosphates as compared to the condensed salts or acids based on elements other than phosphorus. In solutions of any pH at room temperature, or below, the chain and ring phosphates can be studied for several days without noticeable degradation.

A number of factors affect the rate at which chain and ring phosphates undergo hydrolytic degradation in aqueous solution. The major environmental factors are listed here, in what is believed to be their decreasing order of effectiveness:

Factor	Approximate effect on rate
1. Temperature	10^5-10^6 faster from freezing to boiling
2. pH	10^3-10^4 slower from strong acid to base
3. Enzymes	As much as 10^5-10^6 faster
4 Colloidal gels	As much as 10^4–10^5 faster
5. Complexing cations	Very many-fold faster in most cases
6. Concentration	Roughly proportional
7 Ionic environment in the solution	Several-fold change

Study of these factors has been the subject of about 75 papers since the first paper was published in 1852 [52] In spite of the large amount of work on the subject, there are still many problems left to be solved, and indeed items 4 through 7 in the above listing of environmental factors have as yet been only roughly comprehended

The effect of temperature[14,53 59] is probably the best defined of all of the major factors affecting the rate As is the usual case, the variation of the rate constant, k, with temperature can be denoted by the Arrhenius equation

$$k = Ae^{E/RT} \tag{8-23}$$

where the temperature independent term, A, is called the frequency factor; E is called the activation energy; and R and T are the gas constant and the absolute temperature, respectively

It has been found that the activation energy for the splitting of P—O—P linkages in phosphate chains and rings ranges at about 20–40 kcal./mole of linkages, depending on the position of the linkage in the molecule-ion and environmental factors, such as pH, added salt concentration, etc. A good average value is 25 kcal./mole of P —O—P linkages, which is equivalent to doubling the rate for about every 5°C. rise in temperature. With no catalysts (including H^+ and OH^-) present, the activation energy is

[52] A Reynoso, *Ann.*, **83**, 98 (1852), *Compt rend*, **34**, 795 (1852).

[53] G. A. Abbott, *J. Am Chem. Soc*, **31**, 763 (1909), S. J. Kiehl and E. Claussen, Jr, *ibid*, **57**, 2284 (1935).

[54] J. Green, *Ind. Eng. Chem.*, **42**, 1542 (1950); E. Cherbuliez, J. P. Leber, and P. Stucki, *Helv Chim. Acta*, **36**, 537 (1953); also see L. Lutwak and J. Sacks, *J. Biol. Chem.*, **200**, 565 (1953).

[55] S. L. Friess, *J. Am. Chem. Soc.*, **74**, 4027 (1952).

[56] I. A. Brovkina, *J. Gen. Chem.* (*U.S.S.R.*), **22**, 1917 (1953).

[57] J. R. Van Wazer, E. J. Griffith, and J F. McCullough, *J. Am. Chem. Soc.*, **74**, 4977 (1952); *Anal. Chem.*, **26**, 1755 (1954).

[58] D. O. Campbell and M. L. Kilpatrick, *J. Am. Chem. Soc*, **76**, 893 (1954).

[59] J. F. McCullough, J. R. Van Wazer, and E. J. Griffith, *J Am. Chem. Soc.*, **78**, 4528 (1956).

high,[57] around 40 kcal./mole of P—O—P linkages; but this condition is a very rare and idealized situation. There is a drop of 12–17 kcal. in this value when strong acids catalyze the degradation.

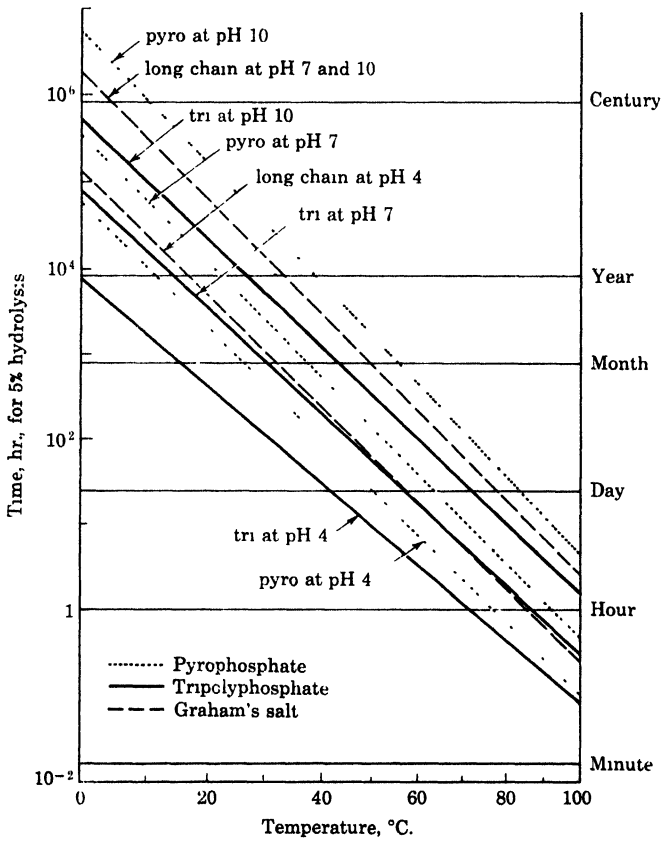


Fig. 8-1. Time for hydrolysis of only 5% of the P—O—P linkages originally present in a 1% solution of chain phosphates at various temperatures Values calculated from references 56, 57, 58, and 59.

It should be observed that items 2–7 in the listing of environmental factors given above describe catalytic effects. At present, information[57,58] is available on the effect of only two of these catalysts (the hydrogen ion and sodium ion) on the temperature dependence of the process of hydrolytic degradation. In these cases, it is found that the catalysts do lower the

activation energy but have their greatest effect on the frequency factor. Presumably this is the case for all of the catalysts listed. A graph showing the effect of temperature on the hydrolysis of chain phosphates is given in Figure 8-1. The time for 5% hydrolysis of the P—O—P linkages originally present is shown in this figure for 1% solutions in water of the normal sodium salts at pH values of 4, 7, and 10.

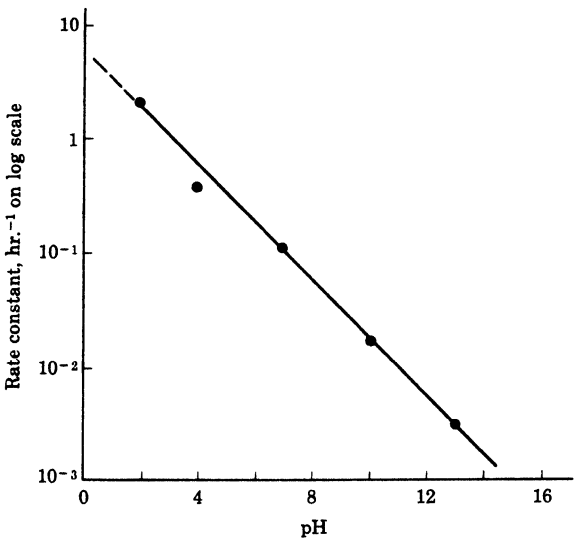


Fig. 8-2. Variation of rate constant[57] for hydrolysis of tetramethylammonium tripolyphosphate with change in pH at 90° in a 0.65 *N* solution sodium bromide.

The hydrolytic degradation of all chain and ring phosphates is strongly catalyzed by hydrogen ions. Therefore, the rates in acidic media are orders of magnitude faster than in neutral solution. This is illustrated by the data[57] of Figure 8-2. This logarithmic dependence of the rate on pH appears to be a rather general phenomenon in the acidic region.[57–60] The addition of a swamping electrolyte to acidic solutions of chain phosphates causes a small diminution in the rate of hydrolysis.[55,57] According to the Bronsted-Bjerrum rule,[61] this indicates a reaction between negative

[60] J. P. Crowther and A. E. R. Westman, *Can. J. Chem.*, **32**, 42 (1954).

[61] J. N. Bronsted, *Z. physik. Chem.*, **102**, 109 (1922); *ibid.*, **115**, 337 (1925); and N. Bjerrum, *ibid.*, **108**, 82 (1954).

and positive ions and leads to the conclusion that the rate is catalyzed by hydrogen (hydronium) ions.

It is also known[56,62–64] that the hydrolysis of ring phosphates is about as strongly catalyzed by hydroxyl ion as by hydrogen ion. This means that ring phosphates hydrolyze to chains very rapidly in strong alkali, but that the chains are then quite stable. Thus, a nearly quantitative yield of tetrapolyphosphate can be obtained by hydrolyzing tetrametaphosphate in alkali.[65] The reported[60,66] increase in the rate of hydrolysis of sodium tripolyphosphate upon the addition of sodium hydroxide does not appear to be due to hydroxyl ion catalysis but, rather, is attributed[58] to catalysis by sodium ion.

The enzymatic hydrolysis of chain and ring phosphates can be extremely rapid under the right conditions.[67] There seems to be little doubt but that enzymes which catalyze the hydrolysis of long chains will not affect the short ones and *vice versa*.[68] Also, the muscle enzymes catalyze only the liberation of orthophosphate from adenosine triphosphate, whereas the enzymes from liver and certain plant tissues apparently catalyze the liberation of pyrophosphate from this material.[69] However, there is still much to be learned about the specificity of the various phosphatases which catalyze the scission of P—O—P linkages.

The action of the phosphatases is greatly affected, as might be expected, by the presence of small amounts of certain metal ions and by pH High temperatures and extremes in pH will deactivate the phosphatases. In general, dipositive ions have a pronounced effect on the enzymatic hydrolysis of P—O—P and C—O—P linkages; and, indeed, no catalysis by phosphatases will occur without the presence of such cations - -especially magnesium. In spite of the fact that enzymatic hydrolysis of the condensed phosphates is extremely fast under optimum conditions, chance microbiological contamination of phosphate solutions will not cause unduly rapid hydrolysis if the concentration of the solutions is reasonably high (> about 1%). However,

[62] K. Karbe and G. Jander, *Kolloid-Beih.*, **54**, 1 (1942)

[63] E. Thilo and R. Rätz, *Angew. Chem.*, **260**, 255 (1949).

[64] R. N. Bell, L. F. Audrieth, and O. F. Hill, *Ind. Eng. Chem.*, **44**, 568 (1952).

[65] W. Faber, *Ger Pat.* 734,511 (1953); G. B. Hatch, U S. Pat. 2,365,190 (1944).

[66] R. Watzel, *Die Chemie*, **55**, 356 (1942)

[67] For a review of the various phosphatases, see J. B. Sumner and K. Myrbäck, *The Enzymes*, Academic Press, New York, 1951, Vol. I, Chapt. 11 (by J. Roche), pp. 473–510; Chapt. 12 (by B. Ingelman), pp 511–16; Vol. II, Part 1, Chapt. 46 (by S. P. Colowick), pp. 114–50; Chapt. 47 (by H. M. Kalckar), pp. 151–61.

[68] B. Ingelman and H. Malmgren, *Acta Chem. Scand.*, **1**, 422 (1945); *ibid.*, **2**, 365 (1948); *ibid.*, **3**, 157 (1949); *ibid.*, **3**, 1331 (1949).

[69] H. M. Kalckar, *Die Chemie*, **2**, Part 1, 152 (1900).

unless special care is taken to insure that the system is sterile, solutions of phosphates in the parts per million concentration range undergo very rapid hydrolysis because of the action of the phosphatases liberated by microorganisms.[70]

The effect of colloidal gels such as the hydrated oxides of iron, cobalt, nickel, aluminum, and the rare earths in accelerating the hydrolytic degradation of chain and ring phosphates is very great.[71] This effect has only been studied by one group of investigators and should be looked into further.

A recent study of the hydrolysis of pyro- and tripolyphosphates showed that the usual increase in rate at higher pH values (10–13) was absent when the system (including the added base) contained no cations except tetramethylammonium ions.[57] Furthermore, substitution of tetramethylammonium by sodium in neutral and alkaline solutions (where the catalysis by hydrogen ion did not overshadow the effect) caused a several-fold increase in hydrolysis rate. This is attributed to the complexing effect of the sodium ion. Calcium ion gives a considerably greater increase in hydrolysis rate than does sodium;[53] but it is reported that magnesium retards hydrolysis without visible formation of a precipitate.[53] This effect is worthy of considerably more study.

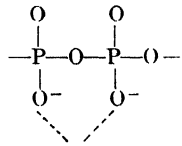
The hydrolysis of pyro- and tripolyphosphates appears to truly be a first-order process so that the rate is exactly proportional to concentration.[57,60] There are reports in the literature that the rate of hydrolysis of chains increases somewhat less than in proportion to the concentration,[72] and, amazingly enough, trimetaphosphate hydrolysis is said to accelerate with decreasing concentration even though the process appears to be first order.[62] Presumably, there are several opposing effects which masquerade under the term "concentration."

The effect of ionic environment is difficult to separate from the other environmental factors, especially the effect of complexing cations. It is believed that this has been done only in a single study.[57] In this case, the ionic environment acted according to the Bronsted-Bjerrum rule, as would be expected. According to this rule,[61] addition of a swamping electrolyte should accelerate phosphate hydrolysis which is catalyzed by positive ions, such as hydrogen, sodium, and calcium. The reverse effect should be found for hydroxyl ion catalysis.

The mechanism of the hydrolysis of the low molecular weight phosphates

[70] E. Karl-Kroupa, C. F. Callis, and E. Seifter, *Ind. Eng. Chem.*, **49**, 2061 (1957).
[71] E. Bamann and M. Meisenheimer, *Ber.*, **71B**, 2086 (1938); *ibid.*, **71B**, 2233 (1938).
[72] D. Balareff, *Z. anorg. u. allgem. Chem*, **68**, 266 (1911); *ibid.*, **72**, 85 (1911).

is relatively straight forward. Simultaneous scissions of P—O—P linkages in the same molecule ion do not occur, and the activated complex is thought to be due to a chelation of the water, hydronium ion, or hydrated metal ion (catalyst) with a



group[73] or the activated complex may involve[15] the *d*-orbitals of the phosphorus so that there would be five bonds proceeding from this atom in the activated complex.

Some authors[58,74,75] have interpreted the effect of pH on the over-all rate of hydrolysis of the pyrophosphate ion as a composite of the rates of hydrolysis of the specific ions: $H_3P_2O_7^-$, $H_2P_2O_7^{3-}$, $HP_2O_7^{3-}$, and $P_2O_7^{4-}$. This is a noble effort which will be practically impossible to extend to longer chains or to rings. Furthermore, it tends to play down the role of the activated complex and to disguise the over-all rate.

The hydrolytic degradation of long chains presents a very difficult theoretical problem. Thilo *et al.*[76] have shown that small rings form as the long chains hydrolyze, and this result is the subject of considerable speculation and study at the time of this writing. The question is how do the long chains curl around in order to split off small rings (trimeta and tetrameta) and why small rings instead of the equivalent chains? Solution of this problem will throw considerable light on the structure of the activated complex.

By going from boiling acid solutions to neutral or slightly basic solutions near their freezing point, the half-life of the phosphates with respect to hydrolytic degradation ranges from the order of minutes to the order of centuries. The slow rate of hydrolysis in netural solution at room temperature or below is emphasized here because of the numerous reports[77] which have dealt exclusively with the easily measurable hydrolysis in acidic solutions at high temperatures. A superficial perusal of the literature gives

[73] E. J. Griffith, unpublished Monsanto report.

[74] J. Muus, *A. physik. Chem.*, **159A**, 268 (1932).

[75] J. D. McGilvery and J. Pedley Crowther, *Can. J. Chem.*, **32**, 174 (1954).

[76] E. Thilo, *Chem. Tech. (Berlin)*, **4**, 345 (1952); E. Thilo, G. Schulz, and E. M. Wichmann, *Z. anorg. u. allgem. Chem.*, **272**, 182 (1953); phenomenon first observed but not interpreted by R. N. Bell, *Ind. Eng. Chem.*, **39**, 136 (1947). Also see ref. 59.

[77] For example, R. A. Morgen and R. L. Swoope, *Ind. Eng. Chem.*, **35**, 821 (1943), and R. W. Atteberry and D. S. Herr, *ibid.*, **37**, 199 (1945).

the impression that the phosphates are much less stable than they really are. The hydrolysis of pyrophosphates, tripolyphosphates, Graham's salt, and the trimeta- and tetrametaphosphates will be discussed individually in their respective places in Chapters 10, 12, and 11.

Condensation in Solution

The very first paper on hydrolysis of condensed phosphates showed that at high temperatures the condensed phosphates degrade completely to orthophosphates.[52] Although most workers in the field have made no particular effort to demonstrate that orthophosphate is the sole product of hydrolysis and that there is not a measurable equilibrium between it and the more condensed forms, the literature does contain considerable data to demonstrate this point. However, there have been several papers[78] which indicate that there is condensation of phosphates in reasonably dilute solution (where R including $H_2O >> 3$). It is presumed that these studies were in error, since they have not been reproduced. In the work by Roche, about 20% of a saturated solution of disodium phosphate was said to be transformed into pyrophosphate by the catalyzing action of an aqueous extract of dog intestinal mucosa. In a recent careful study,[79] it was concluded that the amount of pyrophosphate in equilibrium with orthophosphate in reasonably dilute aqueous solutions is undetectably small, even though the reaction was enzymatically catalyzed.

ASSOCIATION OF PHOSPHATES WITH CATIONS IN SOLUTION

Weakly Acidic Hydrogens

All of the phosphates, including the orthophosphate, are highly charged anions and exhibit the properties of such ions. In addition, the long chain phosphates are typical polyelectrolytes.[80] Because of their high charge, the phosphates tend to associate strongly with cations in all but the most dilute solutions.[81] Accompanying this simple ion association based on electrostatic attraction is a ready tendency to form covalent bonds, probably due to resonance with the π-bonding in the PO_4 groups. The interaction between the hydrogen ion and the phosphates is a good example of ion association with appreciable covalent bonding. A series of titration curves[12]

[78] J. Roche, *Helv. Chim. Acta*, **29**, 1253 (1946); J. Roche, N. van Thoal, and E. Danzas, *Compt. rend.*, **220**, 834 (1945); also see ref. 49.

[79] O. Meyerhof and P. Oesper, *Arch. Biochem. and Biophys.*, **38**, 237 (1952)

[80] For a review of polyelectrolytes see P Doty and G Ehrlich, *Ann. Rev. Phys. Chem.*, **3**, 81 (1953).

[81] F. T. Wall, H. Terayama, and S. Techamkumpuch, *J. Polymer Sci*, **20**, 477 (1956)

for chain and ring phosphates is given in Figure 8-3, from which it should be noted that there is one strong hydrogen ($K_{dissoc.} \approx 10^{\circ}$ to 10^{-3}) for each phosphorus atom. In the case of chain compounds, there is also a weak hydrogen ($K_{dissoc} \approx 10^{-7}$ to 10^{-9}) at either end of the chain. The combination of the strong and weak hydrogens results in the inflection points in the titration curves at pH values near 4.5 and near 10. In addition, there is an extremely weak third hydrogen on orthophosphoric acid ($K_{dissoc} \approx 10^{-13}$), a hydrogen which is too weak to titrate. The presence of a real bond with covalent character holding the weakly acidic hydrogen to the oxygen of the PO_4 groups is graphically demonstrated by the chemical shift

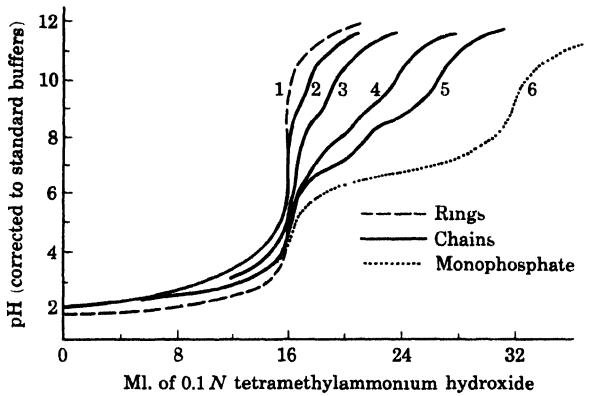


Fig. 8-3. pH titration of a number of phosphates. (1) Trimeta- and tetrametaphosphoric acids; (2-4) acids from vitreous sodium phosphates, (5) tripolyphosphoric acid, and (6) orthophosphoric acid

found in the nuclear magnetic resonance spectrum of the phosphates.[10] In this work, a positive shift of 4–5 p.p.m. of the magnetic field was found when trisubstituted (normal) orthophosphates were converted to orthophosphates having one to three hydrogens per phosphorus atom or when doubly substituted end groups were converted to end groups having one or two hydrogens per phosphorus atom

There are several features[12] of the pH titration curves in Figure 8-3 which should be specifically pointed out First of all, the ring acids are the strongest of all of the phosphoric acids, titrating like hydrochloric acid. On the other hand, the pure chain acids exhibit about the same pH as that of orthophosphoric acid. However, if the one hydrogen per phosphorus atom is partially neutralized, the longer chain acids are found to act as if they were becoming weaker as neutralization proceeds, with the

apparent strength of the acid at a given amount of partial neutralization increasing for shorter chain lengths. This effect, in which the titration curves of long chain phosphates rise higher but less abruptly at the first neutralization point than do the titration curves of the short chain acids, is attributable to ion association due to electrostatic attraction, such as is described below for sodium (see Fig. 8-4).

The second especially noteworthy feature of the titration curves is that the pyro- and tripolyphosphoric acids exhibit three inflection points in their titration curves, a pronounced one near pH 4.5, a small one near pH 7, and a pronounced one near pH 10. This means that when a weakly acidic hydrogen is removed from one end of a short chain phosphate, the hydrogen at the other end becomes even more weakly acidic, since the over-all charge of the anion has been increased For pyrophosphoric acid, there is a difference between the dissociation constants for each of the four hydrogen atoms ($K_1 = 0.1$, $K_2 = 0.01$, $K_3 = 2.7 \times 10^{-7}$, and $K_4 = 2.4 \times 10^{-10}$), and it is K_3 and K_4 which lead to the breaks in the titration curves near pH 7 and pH 10, respectively. For the long chain phosphates, there is only one break in the titration curve, the one near pH 10. Presumably, the anion is already so highly charged (with the charge partially nullified by bound cations) that the removal of a weak hydrogen at one end of the chain does not affect the strength of the hydrogen at the other end, thus making the dissociation constants for both of these hydrogens essentially the same.

It should be noted that the existence of the weakly acidic hydrogen (corresponding to the break near pH 10 in the titration curve) only at the ends of phosphate chains - regardless of the chain length—is an unequivocable argument to show that the weakness of these terminal hydrogens is due primarily to covalent bonding. If the weakly acidic character of the hydrogens were attributable to electrostatic attraction, a large proportion of the hydrogens at other positions in a long chain should be considerably weaker than the terminal hydrogens of a short chain; but this is not the case, as is clearly shown by inspection of the titration curves.

Complexing of Metal Ions

A number of important industrial applications for the chain phosphates are based upon their ability to form soluble complexes with metal ions Again, the complexing of most metal ions probably involves both ionic and covalent contributions to the over-all bond, with the amount of ionic character ranging from practically 100% for sodium[82] to a considerably smaller

[82] C. F. Callis and J. R. Van Wazer, *Advances in Chelate Chemistry*, eds. H. P. Gregor and W. C. Fernelius, John Wiley & Sons, Inc., to be published.

value for the transition group elements, such as iron and cobalt. The ring phosphates also complex metal ions but not sufficiently strongly so that this property is of practical value. And even the orthophosphate ion is a relatively good complexing agent, especially with iron. Thilo[83] has recently pointed out the close similarity between the action of polyphosphates (and, of course, other polyelectrolytes) in solution and solid ion exchange materials. Although this concept of polyelectrolytes as "dissolved ion exchangers" contributes nothing to the over-all picture, it does emphasize the fact that polyelectrolytes either in dissolved or solid forms (as in cross-linked resins) exhibit the same general type of complexing ability toward counter ions.

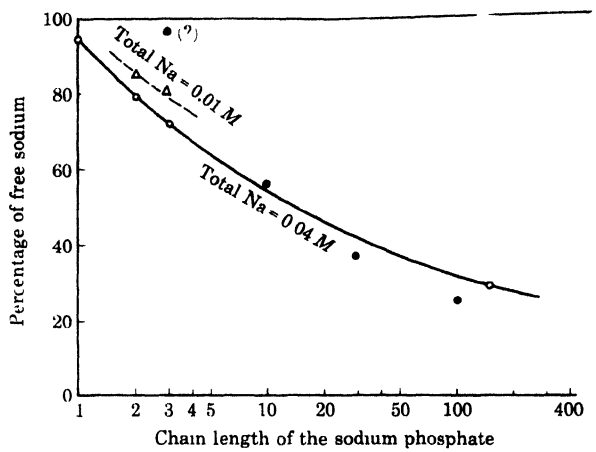


Fig 8-4 Degree of dissociation of the sodium salts of chain phosphates in solution O = transference number, Doremus and Wall;[84] C = 0.04 M in sodium. Δ = transference number, Doremus and Wall;[84] C = 0.01 M in sodium ● = conductivity and transference data, Schindewolf;[85] C = 0.01 M in sodium

The binding of sodium by the chain phosphates has been studied by a number of different techniques. In Figure 8-4, data are given for the binding of sodium by the chain phosphates as determined from two sets[84,85] of

[83] E. Thilo, *Angew. Chem.*, **67**, 141 (1955).

[84] F T. Wall and R. H. Doremus, *J. Am. Chem. Soc.*, **76**, 868 (1954).

[85] U. Schindewolf, *Z. Phys. Chem.* (*Frankfort*), **1**, 134 (1954). It is interesting to note that the first transference measurements made on the condensed phosphates were carried out by Hittorf himself, *Ann.*, **106**, 404 (1859).

electrolyte transference-number measurements and from sodium ion activity measurements with cation exchange membranes.[86] According to this figure, the amount of sodium closely associated with the phosphate chain increases rapidly with the length of the chain in the region below chain lengths of about 30. Above this value, the fraction of the total sodium which is bound to the phosphate chain increases slowly with increasing chain length. The fact that a large fraction of the total counter ions is bound by long chain phosphates is an example of a general phenomenon found for all polyelectrolytes.[87]

The data shown in Figure 8-4 represent the entire amount of sodium bound by the phosphate chains. However, it is possible to differentiate between the various kinds of bound counter-ions, and this has been done for the alkali metals and tetramethylammonium ions by Strauss.[88] In this treatment, the long chain polyphosphate is considered to be in a randomly coiled form. Then the bound counter-ions within the roughly spherical envelope encompassing the coiled chain are apportioned into two classes: those cations which are firmly fixed and those cations which are free to move within the coil. Electrophoresis measurements, which determine the firmly fixed cations,[89] show that the alkali metals are considerably more complexed than the tetramethylammonium ion so that the degree of association, β, in 0.3 M electrolyte solutions is $\beta_{Li} = 66 \times 10^{-2}$, $\beta_{Na} = 69 \times 10^{-2}$, $\beta_K = 59 \times 10^{-2}$, $\beta_{(CH_3)_4N} = 42 \times 10^{-2}$. The order in which these cations are complexed indicates that the close bound alkali metal ions are in intimate contact with the oxygen atoms of the phosphate chain. This is in accord with the nuclear magnetic resonance findings for sodium.[82] It appears that the usual hydration shell of the alkali metal ion is stripped off so that the oxygen atoms on the phosphate chain lie directly against the alkali metal atom, which is not covalently bound but seems to be rigidly held by electrostatic forces (no chemical shift, but an abnormally low resonance peak in the nuclear magnetic resonance spectrum). A schematic diagram of these results is presented in Figure 8-5.

These modern studies on the amount of bound sodium demonstrate the fallacy of much of the literature of the past in which degrees of polymerization of variously prepared metaphosphate compositions were determined

[86] U. Schindewolf and K. F. Bonhoeffer, *Z. Elektrochem.*, **57**, 216 (1953).

[87] For example, J. R. Huizenga, P. F. Grieger, and F. T. Wall, *J. Am. Chem. Soc.*, **72**, 2636 (1950).

[88] U. P. Strauss, D. Woodwide, and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).

[89] F. E. Harris and S. A. Rice, *J. Phys. Chem.*, **58**, 725, 733 (1954); S. A. Rice, *J. Am. Chem. Soc.*, **78**, 5247 (1956), N. Bjerrum, *Kgl. Danske. Videnskab. Selskab*, **7**, No 9 (1926). Also see R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

by colligative measurements.[90] In computing their molecular weights, the authors of this literature usually assumed either no ionization whatsoever or complete ionization of the cations—using no activity corrections in either case. The various mono-, di-, hexa-, and other metaphosphates which have been incorrectly described are explainable in many cases by the fact that the activities and degree of ionization could not properly be taken into account at the period in which the work was done.

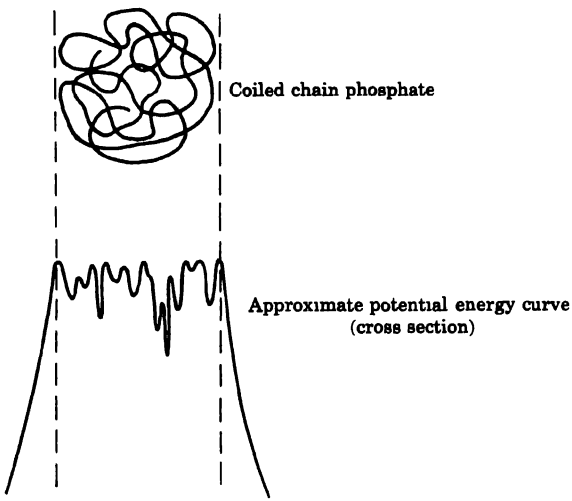


Fig. 8-5. A graphic representation of the shape and force field of a long chain anion, such as polyphosphate, in a salt solution

A polarographic study[91] of the complexing of sodium in a supporting electrolyte of 0.1 *N* tetramethylammonium bromide showed the sodium ion to have a coordination number of two in the complex; and the observed diffusion coefficients indicated that each sodium ion is bound to only one phosphate chain at a time, as might be expected from the two-fold coordination number. Based on this coordination holding a pair of neighboring PO_4 groups in a chain and each such pair of groups being counted in-

[90] Most of this work is reviewed by K. Karbe and G. Jander, *Kolloid-Beih.*, **54**, 1 (1943). Some is also reviewed by D. M. Yost and H. Russell, *Systematic Inorganic Chemistry*, Prentice-Hall Inc., New York, 1944, Chapt. 6, pp. 210–24. Some authors who have misinterpreted colligative data are P. Pascal (a series of papers), S. J. Kiehl, H. Boulle, Mme. Réchid, and others.

[91] J. R. Van Wazer and D. A. Campanella, *J. Am. Chem. Soc.*, **72**, 655 (1950).

dependently of its location in the chain, a pK_{Na} = about 3 was found.[92] Interpretation of pH titration data[91] by the method of Schwarzenbach *et al.*[93] as well as activity measurements[86] using membranes made from cation exchange resins agree in the conclusion that lithium is more firmly bound than sodium, and potassium is somewhat less firmly bound. However, the differences between the three alkali metal ions are not large.

The ability of the phosphates to complex alkaline earth metal ions is very much greater than their ability to complex alkali metal ions. It is because of this that the sodium phosphates can be used in industrial applications for sequestering calcium and magnesium in hard water. Polarographic study[91] of the complexing of barium ion indicates that the barium has a four-fold coordination number, and that often more than one chain phosphate is attached to a given barium ion, so that the barium atoms act to bind a number of chain phosphates together into a loosely knit macromolecule-ion. The dissociation constant for the alkaline earth metals is from 10^2 to 10^7 larger than the dissociation constants for the alkali metals, depending on the exact way the constant is calculated.

In setting up dissociation constants, it is necessary to know the coordination number of the metal ion and the number of sites in the phosphate chain which can be coordinated by the metal, as well as the amount of uncomplex metal as compared to the amount of complexed metal In addition, there are problems in applying the law of mass action to extremely long chains, since a complex toward one end of such a chain will surely not affect the ability to form a complex at the other end of the chain, especially if the chain is so coiled that these two parts are not adjacent to each other. For extremely short chains, the molecular concentration of the phosphate should probably be used in a traditional application of mass action. But if this is done, these numbers cannot be directly compared with dissociation constants obtained on long chains for which independent sites are assumed as a first approximation.

Unfortunately, it is a very difficult job to obtain all of the data needed to define a complex completely, and most investigators assume part of the needed information. This leads to unreal variations and divergencies between the various dissociation constants reported in the literature.[82]

The polarographic data indicated an increase in the binding of barium with the chain length of the phosphate (pK = 4.5 for the pyrophosphate and 6.5 for an average chain length of 75, with these constants being calculated on the basis of two pairs of neighboring PO_4 groups coordinating each barium, the barium exhibiting four-fold coordination).

The complexing of a number of different metals by both chain and ring

[92] This value has also been obtained from e.m.f. measurements with a collodion membrane by F. M. Snell, *Electrochemistry in Biology and Medicine*, ed. T. Shedlovsky, John Wiley & Sons, Inc., New York, 1955, Chapt. 15, pp. 295–7.

[93] G. Schwarzenbach, E. Kampitsch, and R. Steiner, *Helv. Chim. Acta.*, **28**, 828 (1945),

phosphates has been investigated by various procedures,[92] most of which give only qualitative results. However, it does appear that the transition group metals are very strongly complexed and that, in general, the degree of complexing increases with the charge on the metal ion being complexed. Ring phosphates do not complex metal ions as strongly as do the chain phosphates having the same number of phosphorus atoms. In fact, there appears to be approximately a hundred-fold difference in the complexing ability between the two. As yet, nothing is known about the effect on complexing of crosslinking of chain phosphates in which the branching points are stabilized by steric hindrance.

There is some evidence that complexing of metal ions by the phosphates occurs in melts, as well as in aqueous solution.[94] In particular, the absorption bands of colored metal ions are usually found to shift toward the ultraviolet, as compared to their absorption in silicate glasses and in solutions of simple salts of these metal ions. This effect has found application in the manufacture of heat-resistant glasses in which considerable iron is incorporated as an infra-red absorbing agent, with phosphate being used to reduce the color of the silicate-based glass.

Phosphates and Large Cations

Ever since the time of Berzelius,[1] it has been known that certain condensed phosphates will form precipitates with soluble proteins, such as albumin. This action occurs only in acid media and has been the subject of considerable study.[95–97] It now appears that the phenomenon is simply one of cation-anion interaction. At pH values below their isoelectric point, proteins act as high molecular weight cationic electrolytes, the over-all charge of which depends on the exact pH.

In strongly acidic solution the chain phosphates are found to utilize completely the so-called "acid-combining capacity" of the proteins; in other words, the amino groups are all neutralized by the phosphate.[95] This masking of the $—NH_2$ groups of the protein causes a shift in the over-all dissociation constant of the —COOH groups to a pH region in which they

[94] N. J. Kreidl and W. A. Weyl, *J. Am. Ceram. Soc.*, **24**, 372 (1941); G. F. Brewster and N. J. Kreidl, *Trans. Soc. Glass Technol.*, **35**, 332 (1951).

[95] Some important papers are R. K. Schofield, *Trans. Faraday Soc.*, **31**, 390 (1935), G. Perlmann and H. Hermann, *Biochem. J.*, **32**, 926 (1938); D. R. Briggs, *J. Biol Chem.*, **134**, 261 (1940); and G. Perlmann, *ibid.*, **137**, 707 (1941).

[96] For a review of some other work, see A. A. Horvath, *Ind. Eng. Chem., Anal. Ed.*, **18**, 229 (1946).

[97] B. Katchman and J. R. Van Wazer, *Biochim. et Biophys. Acta*, **14**, 445 (1954), also unpublished data.

may be readily titrated. The action of the condensed phosphates on proteins is similar to that of other anions of rather high molecular weight When a relatively small amount of condensed phosphate is used, the addition of neutral salts tends to dissolve the precipitate formed between the protein and the phosphate.

A recent study has shown that the higher the molecular weight of the water-soluble protein, the less of a given phosphate is needed to give a precipitate;[97] and, conversely, the higher the molecular weight of the phosphate, the less of a given protein is needed.[98] At a fixed, highly acid pH, the high molecular weight proteins precipitate long chain phosphates at very low concentrations, but low molecular weight proteins do not precipitate with low molecular weight phosphates even at relatively high concentrations. In other words, the higher the molecular weight of either the phosphate or the protein, the lower the concentration at which the "metaphosphate-protein" reaction occurs.

The ability of the chain phosphates (for which $n >$ about 4) to tan leather[99] is apparently a variation of the phosphate-protein reaction described above. It is found that the longer chain phosphates combine more firmly with the hide than do the chains having less than about 15 phosphorus atoms.

Another similar cation-anion interaction is found in the metachromatic reaction in which high molecular weight phosphates cause a shift in the absorption maxima of certain cationic dyes to lower frequencies.[100] This reaction is the basis of a microscopic staining procedure used for determining which parts of a cell contain high molecular weight phosphates. Studies with toluidine blue have shown that the optical density at 630 mμ decreased and at 530 mμ increased with increasing chain length in the range from $\bar{n}$ = 6–30 and that pyro-, tripoly-, trimeta-, and tetrametaphosphates do not exhibit the metachromatic effect.

The so-called incompatibility of glassy phosphates with the quaternary ammonium salts which are used for germicidal purposes is another example of the precipitation of high molecular weight cations by the chain

[98] This later point is also demonstrated by the earlier literature, *e.g.*, D. Balareff, *Z anal. Chem.*, **73**, 411 (1928).

[99] For a good recent paper, see K. H. Gustavson and A. Larsson, *Acta Chem. Scand.*, **5**, 1221 (1951). Also see *Dept. of Sci. and Ind. Res., Report for the Year* **1952–1953**, London, Feb. 1954, p. 182.

[100] S. P. Damle and P. S. Krishnan, *Arch. Biochem and Biophys.*, **49**, 58 (1954); J. M. Wiame, *J. Am. Chem. Soc.*, **69**, 3146 (1947); also see G. Schmidt, *Phosphorus Metabolism*, eds. W. D. McElroy and B. Glass, Johns Hopkins Press, Baltimore, Md., Chapt. VII, p. 443.

phosphates.[101] In order to achieve a satisfactorily high antimicrobiological action, long chain organic radicals are incorporated into the quaternary ammonium ions. These ions precipitate the commercial glassy phosphates although the same phosphates can be mixed with tetraethyl- or tetramethyl-ammonium salts at high concentrations without precipitation. A recent paper covers the interaction of the long chain phosphates with a number of organic bases of biological interest.[102]

EFFECTS OF PHOSPHATES ON COLLOIDS

As might be expected from their high charge, all of the phosphates in small concentrations greatly affect suspensions of colloidal particles. The chain phosphates are well known as peptizing, deflocculating, and dispersing

TABLE 8-7

Data[104] from Cataphoresis Studies on Clays Suspended in Liquors Obtained from Centrifuging 45 Per Cent Clay Slurries

(Deflocculants present in slurry to extent of 5.0 milliatomic weights (of phosphorus) per 100 g of dry clay)

Deflocculant added	Cataphoretic velocity (μ/sec. at 1 v/cm)	Calculated zeta potential (mv)	Appearance of clay in microscope (magnification 120×)
	Clay: sodium kaolin, pH = 7.0		
None	−5.0	−71	Flocs in clear liquid
Sodium chloride	−5.1	−72	As above
Sodium orthophosphate	−7.7	−109	Some small flocs
Sodium trimetaphosphate	−6.6	−93	Many very small flocs
Sodium pyrophosphate	−8.1	−114	Some very fine flocs
Glass: $7\ Na_2O \cdot 5\ P_2O_5$ ($\bar{n}$ = 5.0)	−9.2	−130	Unresolved milky liquid
Glass: Na_2O, P_2O_5 ($\bar{n}$ = 200)	−9.6	−135	As preceding sample
	Clay: calcium kaolin, pH = 7.0		
None	−2.4	−34	Very large flocs
Sodium chloride	−3.7	−52	Large flocs
Glass: $7\ Na_2O \cdot 5\ P_2O_5$ ($\bar{n}$ = 5.0)	−9.4	−133	Unresolved milky liquid

[101] R. Neu, *Z. anal. Chem.*, **131**, 102 (1950); *Fette u. Seifen*, **53**, 148 (1951); *ibid.*, **54**, 682 (1952); *ibid.*, **55**, 17 (1953); *ibid.*, **56**, 298 (1954).

[102] J. P. Ebel, *Bull. soc. chim. biol.*, **37**, 445 (1955).

agents. The action of the chain phosphates as detergent builders is also attributable in part to their charge, which aids in salting out and stabilizing micelles of organic surfactants. Even the orthophosphate ion is strongly adsorbed on surfaces; and the chain phosphates are considerably more strongly adsorbed. An interesting application of this property is found in "threshold treatment"[103] in which the formation of calcium carbonate crystals is inhibited by adsorption of chain phosphates on the calcite crystal nuclei forming in hard water

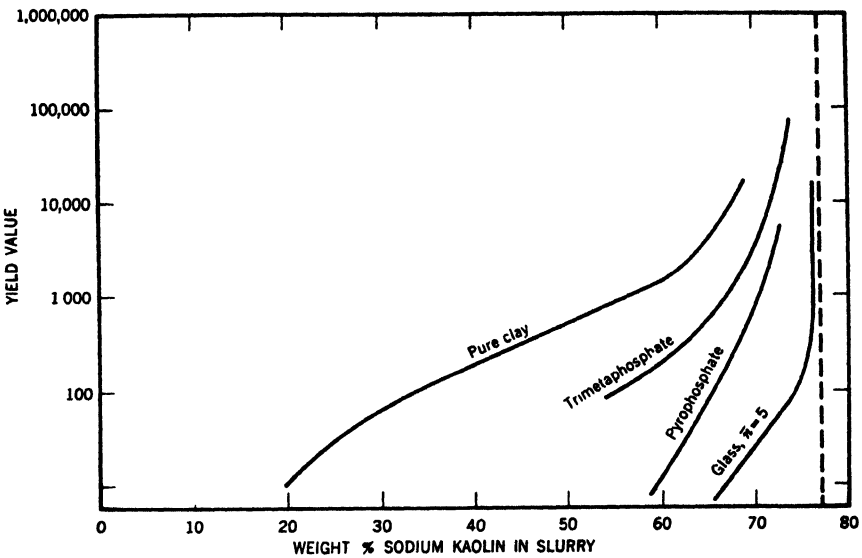


Fig. 8-6. Variation of measured yield value with amount of dry sodium kaolin slurried with water.[104] Phosphates present in amount of 5 mg./100 g. dry clay; upper limit of plasticity at dotted line.

Measurement of the cataphoretic velocity of clay particles suspended in dilute solutions of various salts shows that the long chain phosphates cause a considerable negative increase in the zeta potential of the particles.[104] These data are reported in Table 8-7. The deflocculating action

[103] R. F. Reitemeier, *J. Phys. Chem.*, **44**, 535, 552 (1940); B. Raistrick, *Discussions Faraday Soc.*, **5**, 234 (1949); R. F. Reitemeier and A. D. Ayers, *J. Am. Chem. Soc.*, **69**, 2759 (1947); M. Breton, *Bull. soc. chim. France*, **1947**, 297; H. W. Douglas and R. W. Walker, *Trans. Faraday Soc.*, **46**, 559 (1950).

[104] J. R Van Wazer and E. Besmertnuk, *J. Phys. Colloid Chem.*, **54**, 89 (1950); T. F Ford, A. G. Loomis, and J. F. Fidiam, *J. Phys Chem.*, **44**, 1 (1940).

of the phosphates is graphically illustrated by measurement of the yield value of concentrated clay slurries which are so thick that it takes a considerable force to deform them [103] The plastic properties of untreated clay can be measured by the width of the concentration region in which there is a moderately high and relatively constant yield value a region ranging over about 35–60% solids for undeflocculated sodium kaolin as shown in Figure 8-6 This plastic region is caused by the fact that the individual clay particles attract each other so that they agglomerate in the concentrated slurry, leaving many large interstices between agglomerates The strength of this house-of-cards type of structure is not very dependent on the size of the voids; and, hence, the yield value of the untreated clay changes only gradually over a considerable concentration range When ions are strongly adsorbed on the clay particles, the resulting high surface charge causes the particles to repel each other so that they can no longer build a house of cards. This means that the slurry will flow very readily at all concentrations below the point at which the individual clay particles fill nearly the entire volume of the slurry and there are few liquid-filled voids left between them This thinning of the slurry is exactly what happens when plastic masses of clay are treated with phosphates, as shown by Figure 8-6 which indicates that ring phosphates are not so good deflocculants as chain phosphates and that the best deflocculation is obtained with the longer chains When a long chain phosphate is used in the amount of a few tenths per cent of the weight of the dry clay, the plastic region of the resulting slurry completely disappears. As the water content is reduced, there is finally a rapid transition from a free-flowing slurry to a crumbly mass as the solids concentration is raised to about 70–75% of the slurry The dotted perpendicular line in Figure 8-6 corresponds to a close packing of the clay particles. At solid concentrations to the right of this dotted line, there is insufficient water to fill all the interstices between the closely packed clay particles, and the clay-water mass is no longer cohesive under any conditions

Study[103] of the threshold-treatment effect has shown that the rate of nucleation of calcite crystals is extremely low in hard water containing a few parts per million of a chain phosphate. When the calcite crystals do finally form, they exhibit rounded, very misshapen faces. The phenomenon is purely one of adsorption on the crystal nuclei, since the activity of the dissolved calcium ions is not appreciably affected by the extremely small amount of added chain phosphate. Ring phosphates are ineffective in this application.

Control[105] of corrosion of metal surfaces exposed to natural waters by the use of a trace amount of a chain phosphate appears to be related to the threshold-treatment effect. Protection of the metal surfaces is achieved by cathodic control believed to be due to an adherent thin coating of calcite which is inhibited from growing to noticeable thickness by the adsorption of the chain phosphates. These phosphates do not inhibit corrosion in distilled water free from calcium; and it is also found that the ring phosphates are ineffective

ELECTRICAL, MECHANICAL, AND OPTICAL PROPERTIES OF PHOSPHATE SOLUTIONS

The low molecular weight phosphates exhibit the properties that might be normally expected from highly charged ions However, the long chain phosphates also show properties that depend on their thread-like structure. For example, the chain phosphates exhibit optical birefringence[106] and anisotropic electrical conductivity[107] when made to flow. Both the optical and the electrical anisotropy increase with chain length and decrease upon the addition of low molecular weight salts which cause the chains to coil. The evidence of both the optical and the electrical measurements is that the chains line up in the direction of flow. A similar alignment can be achieved by passing an alternating electric current through a solution of long chain phosphates [108] In this case, the chains again tend to line up in the direction of the flow of current. Then conductivity measurements carried out in this direction and at right angles to it show that the conductivity in the direction in which the alternating current had been flowing is greater than normal, and the conductivity at right angles to this direction is smaller than normal Rotary diffusion constants for the chains can be calculated from these three kinds of measurements, and the values so obtained are in accord[106] with the straight-chain model of the phosphate studied.

Because of the binding of sodium ions with increasing chain length, the transference number of the chain phosphates, as measured by the standard Hittorf technique,[85] increases with increasing chain length and finally approaches a limiting value of about 2.1 for very long chains. Such transference numbers give no information as to the distribution of the total

[105] G B. Hatch and O Rice, *Ind Eng Chem*, **31**, 51 (1939); **32**, 1572 (1940), **37**, 710 (1945), B Raistrick, *Chemistry & Industry*, **1952**, 408

[106] J. R. Van Wazer, M Goldstein, and E. Farber, *J. Am. Chem. Soc.*, **74**, 4977 (1952)

[107] U. Schindewolf, *Z physik. Chem. (Neue Folge)*, **1**, 9 (1954); *Naturwissenschaften*, **16**, 435 (1953).

[108] M Eigen and G. Schwarz, *Z. physik. Chem. (Frankfurt)*, **4**, 380 (1955)

current between the cation and the anion; but the values do show that, as a result of association, relatively more phosphorus in the long chain phosphates is transported to the anode by a given amount of current than would be possible for a complete dissociated electrolyte. When the measured transference number of the phosphate is greater than unity, the transference number of the counter-ion must be negative; *i.e.*, the cations must also be carried to the anode The data shown in Figure 8-7 for the transference number of the chain phosphates are somewhat similar to the plot of the transference number of cadmium in cadmium iodide, which at high

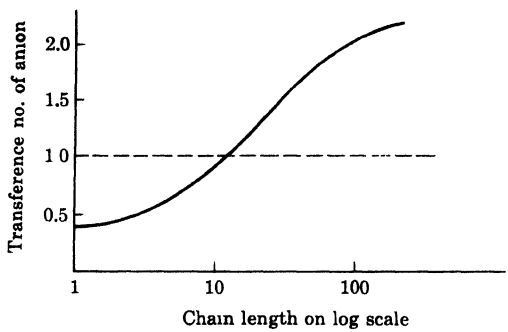


Fig. 8-7. Hittorf-type transference numbers of the phosphate anion as a function of chain length of chain sodium phosphates. When the values exceed unity (dotted line), sodium is building up at the anode as electrolysis proceeds Concentration in all cases is 0 01 equivalent of sodium per liter

concentrations also exhibits an anomalously large transference number because of formation of the CdI_4^{2-} complex.

In Figures 8-8 and 8-9, the equivalent conductivity of the chain and ring phosphates are plotted as a function of concentration The plot[109] of Figure 8-8 is the usual one in which the concentration is reported in terms of its square root, so as to fit the Onsager limiting law. However, for polyelectrolytes, this law no longer holds, and it is believed that the change with concentration should be approximately logarithmic Such a logarithmic plot is presented in Figure 8-9 for a series of phosphate glasses ranging in chain length from 5.8 to 52 and a sample of Kurrol's salt exhibiting an average chain length of 1000.[84,85]

The measurement of the viscosity number, $(\eta_{soln} - \eta_{solvent})/C\eta_{solvent}$, at low concentrations has served as a good tool for unraveling the structure of

[109] C. W. Davies and C. B. Monk, *J. Chem. Soc.*, **1949**, 413, 423, 427.

the chain phosphates.[14,110–112] As is the general case for flexible polyelectrolytes, the viscosity number of the phosphates is accurately represented by the Fuoss equation.[113]

$$\frac{\eta_{soln} - \eta_{solvent}}{C\eta_{solvent}} = \frac{A}{1 + B\sqrt{C}} + D \qquad (8\text{-}24)$$

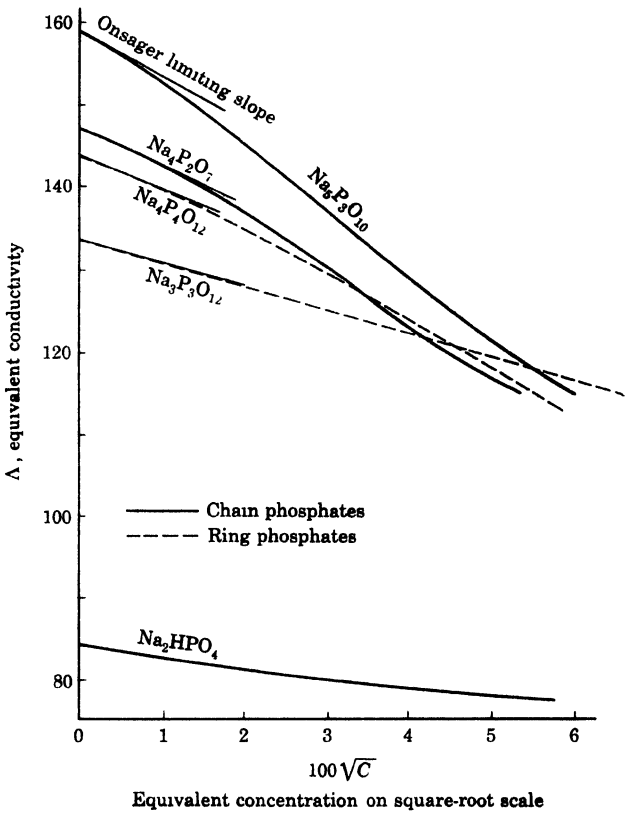


Fig 8-8 Equivalent conductivity of some sodium phosphates as a function of the square root of the sodium ion concentration in atomic weights per liter.

[110] U. P. Strauss and E. H. Smith, *J. Am. Chem. Soc.*, **75**, 6186 (1953).

[111] J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 906 (1950); also see ref. 59

[112] H. Malmgren, *Acta Chem. Scand.*, **2**, 147 (1948), *ibid.*, **6**, 1 (1952)

[113] R. M. Fuoss, *J. Polymer Sci.*, **3**, 603 (1948); *ibid.*, **4**, 96 (1949); R. M. Fuoss and U. P. Strauss, *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949); H. Terayama and F. T. Wall, *J. Polymer Sci.*, **16**, 357 (1955).

The parameters of this equation increase in an approximately linear manner with chain length for the molecular weight range studied.[107] Thus, for a weight-average chain length of 50, as determined by light scattering, A is very small, B = about 18, and D = about 0.05; whereas, for a weight-

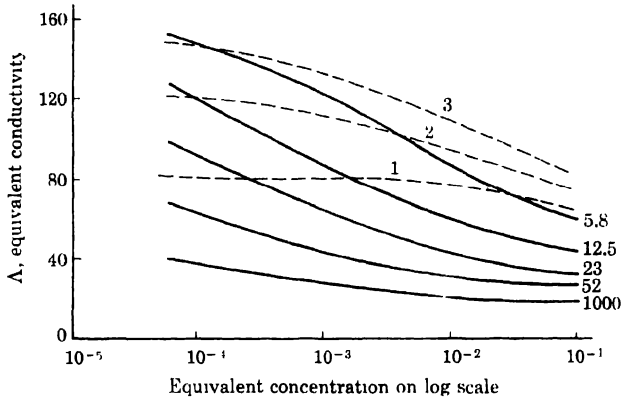


Fig. 8-9. Equivalent conductivity of chain phosphates as a function of the logarithm of the sodium ion concentration in atomic weights per liter. The numbers to the right of each curve give the number-average number of phosphorus atoms per phosphate chain. Dotted lines refer to (1) ortho-, (2) pyro-, and (3) tripolyphosphates.

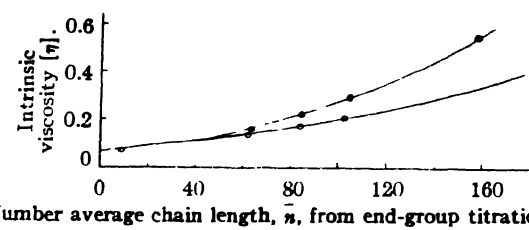


Fig. 8-10. Variation of intrinsic viscosity of the usual slightly branched and straight chain phosphates from Na_2O/P_2O_5 glasses as a function of chain length. Zero-time extrapolated values for chains with some branching denoted by black circles; values after 12-hr. standing (with chain lengths corrected for ortho) by open circles.

average chain length of 200, A = about 22, B = about 40, and D = about 0.12, when C is measured in grams of phosphate/100 ml. of solution. In the presence of a large amount of added simple salt, the chain phosphates coil and start to obey the usual relationship for the limiting viscosity number of uncharged high polymers. A plot of this type of relationship is given

in Figure 8-10 for straight chain polyphosphates.[110, 111] This plot can be used to determine the molecular weights of long chain phosphates.

The viscosities of chain phosphates in concentrated solution are Newtonian up to chain lengths of about 500. However, the longer chains in which there are several thousand phosphorus atoms begin to show pseudoplastic behavior in flow. This is also true of the steric-hindered, crosslinked phosphates. But the flow properties of all of the chain phosphates produced to date can be closely approximated by a single viscosity coefficient for any one temperature or concentration; *i.e.*, they are essentially Newtonian. In highly concentrated solutions of long chain phosphates, elastic properties are noticeable. When considered as plastics, the chain phosphates are found to be plasticized the best by a small amount of water.

A considerable number of molecular weight measurements have been carried out on solutions of chain phosphates, using the ultracentrifuge.[112,114] In this work, both the sedimentation and equilibrium methods of measuring molecular weight were found to correlate with other techniques; but different molecular weights were calculated for different added electrolytes,

TABLE 8-8
Chain Lengths and Other Data as Function of Added Salt Used in Ultracentrifuge Measurements[112]

Kurrol salt preparation[a]	Medium used	Sedimentation constant at infinite dilution (S_0)	Diffusion constant at infinite dilution (D_0)	n Calculated chain length (zeta average)	Molecular symmetry factor (f/f_0)
A	1.1 *N* NaCl	12	0.87	5,400	
	0.4 *N* NaCl	34	1.20	11,000	
	0.2 *N* $Na_4P_2O_7$	12	0.86	5,500	
	0.8 *N* $Na_4P_2O_7$	17	0.98	6,800	
B	0.1 *N* NaCl	14	1.05	4,100	5.2
	0.4 *N* NaCl	32	1.08	9,300	3.8
	0.1 *N* NaCl in 5% ethanol	20	1.25	4,800	4.1
	0.1 *N* NaCl in 8% ethanol	25	1.36	5,500	3.6

[a] These preparations were made by heating KH_2PO_4 for several hours at 500°C.

[114] O. Lamm and H. Malmgren, *Z. anorg. Chem.*, **242**, 103 (1940); *ibid.*, **252**, 256 (1944); also see O. Lamm, *Arkiv. Kemi. Mineral. Geol.*, **17A**, No. 25 (1944); *ibid.*, **18A**, No. 8 (1944).

the electrolyte being used to obviate the problems of interpretation which arise when polyelectrolytes are studied in a pure solvent. A listing of the various molecular weights found for two samples in the presence of several different electrolytes is given in Table 8-8. Presumably, these differences in the observed chain lengths are due to imperfect mathematical treatment of the data. Present-day studies are unearthing many similar anomalies

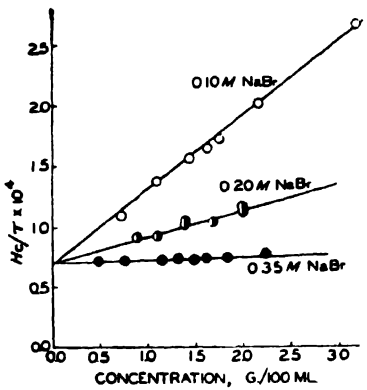


Fig. 8-11. Light-scattering data for a sample of Graham's salt. The intercept at $c = 0$ gives the reciprocal of the weight-average molecular weight which is 14,000

for ionized organic macromolecules which definitely do not change their degree of polymerization and are not believed to form aggregates. At present, only relative sizes of polyelectrolytes are known with certainty, and most measurements are but guesses as to absolute sizes of the molecule-ions of large polyelectrolytes.

Light scattering has also been employed to characterize the chain phosphates as linear, flexible, polydisperse polyelectrolytes. It is found[14] that the light scattering of chain phosphates gives a very good fit to the theoretical equation.[115]

$$\frac{HC}{\tau} = 1/M + 2Bc \tag{8-25}$$

This equation for nonionic polymers whose molecules are isotropic and small compared to the wave length of light is applicable to sodium polyphosphate in sodium bromide solutions, even though it does not apply to polyelectro-

[115] P. Debye, *J. Applied Phys.*, **15**, 338 (1944); P. M. Doty, B. H. Zimm, and H. F. Mark, *J. Chem. Phys.*, **12**, 144 (1944); *ibid.*, **13**, 159 (1945).

lytes under all conditions. In the equation, τ is the excess turbidity of the solution over that of the solvent, c is the concentration of polymer in grams per milliliter of solution, and

$$H = \frac{32\pi^3 n_0^2}{3N_0\lambda^4}\left(\frac{n - n_0}{C}\right)^2$$

where N_0 is Avogadro's number, λ is the wave length of the light, and n_0 and n are the refractive indices of solvent and solution, respectively. M is the molecular weight, and B is a constant which depends on the interaction of the polymer molecules with one another. The results that Strauss *et al.*[14] obtained for one sample of Graham's salt are shown in Figure 8-11. The lines all have a common intercept, which is the reciprocal of the molecular weight of the sample.

At the present time it appears that light scattering and pH titration for end groups[116] are the most reliable methods for determining the average molecular weights of the longer chain phosphates. In intercomparing molecular weights obtained by various methods,[117] it should be remembered that end-group titrations and colligative measurements give number-averages, viscosity numbers give so-called "viscosity" averages (between number and weight-averages), light scattering gives weight-averages, and ultracentrifuge measurements normally give zeta averages (although the number- and weight-averages can also be calculated from ultracentrifuge data). The application of polymer physics to chain phosphates has been the subject of a review.[118]

[116] O. Samuelson, *Svensk. Kem. Tid.*, **56**, 343 (1944), **61**, 76 (1949); also see refs. 12 and 37.

[117] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, Chapt. 8, pp. 317–98.

[118] C. F. Callis, J. R. Van Wazer, and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954).

CHAPTER 9

Orthophosphoric Acid, Its Salts and Esters

HISTORY

The orthophosphates were known to primitive man in the form of bones and colorful minerals such as turquoise. The alchemists used bones and other phosphatic material, such as urine, in many of their operations and undoubtedly prepared a number of orthophosphates of varying degrees of purity. Perhaps the crystalline phosphate best known[1] to the alchemists was microcosmic salt, sodium ammonium orthophosphate, $Na(NH_4)HPO_4 \cdot 4\ H_2O$. Phosphoric acid was first described by Robert Boyle,[2] who showed that the action of water on the products of combustion of phosphorus gave a liquid with acid properties.

ORTHOPHOSPHORIC ACID

General Behavior of the Orthophosphate Ion

The orthophosphates of the alkali metals, ammonia and the lower molecular weight substituted ammonium ions, are all quite soluble in water, except for trilithium orthophosphate. On the other hand, the orthophosphates of the multiply charged or heavy metals are all relatively insoluble. A large number of crystalline orthophosphates are known, and, indeed, the orthophosphate ion is often found as a unit in highly complicated crystals which contain a number of cations and sometimes several other anions. Almost all of the many phosphate minerals are orthophosphates, and quite

[1] For example, Geber, *Liber investigationis magisterii*, Strassburg, 1598; J. I. Hollandus, Tractatus de urina, *Theatrum chemicum*, **6**, 566 (1661); J. B. van Helmont, *De lithiasi*, Francofurti, 1682. During this period the salt, which was obtained from urine, was called *sal urinae fixum* as compared to *sal urinae volatile*, the alchemical name for ammonium carbonate. The term *sal microcosmicum* was used by Paracelsus, who gave it this name because it came from human urine. Man was supposed to be a miniature universe (microcosm) by some alchemists.

[2] R. Boyle, *Phil. Trans.*, **13**, 196, 428 (1680).

a few of them represent fine examples of the complicated crystals referred to above (see Appendix A for a listing of minerals). From the viewpoint of structural chemistry, there are two limiting kinds of crystalline orthophosphates. One is the kind of crystal in which the PO_4 groups exhibit three negative charges apiece (isolated PO_4 groups); and the other is a three-dimensionally bonded crystal in which the oxygen atoms share electrons not only with the phosphorus atoms (four-way branching points) but also with those of another element, also surrounded by four neighboring oxygen atoms.

The orthophosphates can often be found as amorphous solid compositions as well as in the form of crystals. Precipitates showing only one or two broad bands when studied by x-ray diffraction can be made by combining a soluble orthophosphate with a soluble salt of a polyvalent metal, such as aluminum or iron. Crystallization in such amorphous materials can often be induced by digestion or by acidifying and then gradually raising the pH. Many of these amorphous compositions, as well as some of the crystalline phosphates of polyvalent metals, can be readily produced as colloidal dispersions. When prepared in the proper manner, orthophosphates of some of the multiply charged metals form highly viscous solutions in water. It is believed that such solutions contain soluble or partially soluble aggregation polymers, held together by the high charge on the anions and cations.

The orthophosphate ion serves as a good complexing agent for the transition metals, and orthophosphoric acid has long been used to decolorize solutions containing small amounts of ferric iron.

Ionization of Orthophosphoric Acid

Orthophosphoric acid is a tribasic acid which is quite strong with respect to the first dissociation constant, moderately weak with respect to the second, and very weak with respect to the third. The accurate determination of the dissociation constant of an acid as strong as the first hydrogen of H_3PO_4 requires that the hydrogen ion concentration be established with greater accuracy than is usually attainable. This has been done by Bates,[3] who showed that the dissociation constant, K_1, for the first hydrogen, in the temperature range of 0–60°C., is given by

$$-\log K_1 = 799.31/T - 4.5535 + 0.013486T \qquad (9\text{-}1)$$

where T is the absolute temperature (°K.). At 25°C. this leads to a value

[3] R. G. Bates, *J. Research Natl. Bur. Standards*, **47**, 127 (1951).

of $K_1 = 0.7107 \times 10^{-2}$ which agrees approximately with the earlier, carefully determined value [4,5] of 0.752×10^{-2}.

The second dissociation constant[6] of orthophosphoric acid is given by an equation similar to equation 9-1. The following equation is correct for the temperature range of 0–50°C.

$$-\log K_2 = 2073.0/T - 5.9884 + 0.0209127T \qquad (9\text{-}2)$$

At 25°C. this corresponds to a value of $K_2 = 7.99 \times 10^{-8}$. The third dissociation constant,[7,8] K_3, is 4.8×10^{-13} at 25°C. In addition to the work

[4] L. F. Nims, *J. Am. Chem. Soc.*, **56**, 1110 (1934); also see M. Jowett and H. I. Price, *Trans. Faraday Soc.*, **28**, 668 (1932) ($K_1 = 0.65 \times 10^{-2}$); J. W. H. Lugg, *J. Am. Chem. Soc.*, **53**, 1, 2554 (1931) ($K_1 = 0.81 \times 10^{-2}$); S. K. Majumdar, *J. Indian Chem. Soc.*, **8**, 87 (1931) (effect of electrolytes on K_1).

[5] Other papers discussing more than one acid dissociation constant of H_3PO_4 are: J. C. McGowan, *Chemistry & Industry*, **1948**, 632 (1949); *Nature*, **159**, 644 (1947) (free energies of ionization), Yrjo Hentola, *Kemian Keskuslaton Julkarsuja*, **13**, No. 2, 1 (1946) ($K_1 = 0.67 \times 10^{-2}$, $K_2 = 6.1 \times 10^{-8}$, $K_3 = 4.4 \times 10^{-13}$); G. Schwarzenbach, A. Epprecht, and H. Erlenmeyer, *Helv. Chim. Acta*, **19**, 1292 (1936) (dissoc. constants in H_2O and in D_2O); M. Jowett and H. Millet, *J. Am. Chem. Soc.*, **51**, 1004 (1929) ($K_1 = 0.80 \times 10^{-2}$, $K_2 = 7.5 \times 10^{-8}$, $K_3 = 8 \times 10^{-13}$); I. M. Kolthoff, *Rec. trav. chim.*, **46**, 350 (1927) ($K_1 = 0.8 \times 10^{-2}$, $K_3 = 5 \times 10^{-13}$); J. Sendroy and A. B. Hastings, *J. Biol. Chem.*, **71**, 783 (1927) ($K_1 = 0.78 \times 10^{-2}$ at 18°C., $K_2 = 7.1 \times 10^{-8}$ at 38°C., $K_3 = 2.2 \times 10^{-13}$ at 38°C.), E. B. R. Prideaux and A. T. Ward, *J. Chem. Soc.*, **125**, 423 (1924) ($K_2 = 5.9 \times 10^{-8}$, $K_3 = 1.3 \times 10^{-12}$), G. A. Abbott and W. C. Bray, *J. Am. Chem. Soc.*, **31**, 729 (1909) ($K_1 = 1.1 \times 10^{-2}$, $K_2 = 1.95 \times 10^{-7}$, $K_3 = 3.6 \times 10^{-13}$).

[6] R. G. Bates and S. F. Acree, *J. Research Natl. Bur. Standards*, **34**, 373 (1945), *ibid.*, **30**, 129 (1943); other values of the second dissociation constant are given by the following authors: Nobutugu Koyenuma, *Biochem. Z.*, **317**, 204 (1944) ($K_2 = 2.67 \times 10^{-7}$); Kwaniti Sima, *J. Biochem. (Japan)*, **29**, 121 (1939) ($K_2 = 9.6 \times 10^{-8}$); E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 533 (1934) ($K_2 = 5.97 \times 10^{-8}$); L. F. Nims, *J. Am. Chem. Soc.*, **55**, 1946 (1933) ($K_2 = 6.5 \times 10^{-8}$ at 37.5°C.); J. W. H. Lugg, *Trans. Faraday Soc.*, **27**, 297 (1931) ($K_2 = 9.3 \times 10^{-8}$ at 23.5°C.); L. Michaelis and T. Garmendia, *Biochem. Z.*, **67**, 431 (1941) ($K_2 = 8.8 \times 10^{-8}$); also see ref. 5.

[7] N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.*, **9**, No. 1 (1929); also see refs. 5 and 8.

[8] Other values of the third dissociation constant are given by the following authors: N. Konopik and O. Leberl, *Monatsh.*, **80**, 655 (1949) ($K_3 = 1.1$–1.8×10^{-12}); R. C. Wells, *J. Wash. Acad. Sci.*, **32**, 321 (1942) ($K_3 = 3.7 \times 10^{-12}$); F. L. Hahn and R. Klockmann, *Z. physik. Chem.*, Abt. A., **151**, 80 (1930) ($K_3 = 1.3 \times 10^{-12}$); I. N. Kugelmass, *Biochem. J.*, **23**, 587 (1929) ($K_3 = 1.2 \times 10^{-12}$).

reported in references 3 to 8, a number of authors have investigated activity coefficients[9] in orthophosphate solutions.

The heats and free energies of ionization show that the first dissociation of orthophosphoric acid is exothermic, and the following two dissociations are endothermic. The exact values[4,6,10] are given below:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad (9\text{-}3)$$

$\Delta H_{25^\circ} = -1.88$ kcal $\qquad \Delta F_{25^\circ} = +2.90$ kcal

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad (9\text{-}4)$$

$\Delta H_{25^\circ} = +0.99$ kcal $\qquad \Delta F_{25^\circ} = +9.82$ kcal.

$$HPO^{2-} \rightleftharpoons H^+ + PO_4^{3} \qquad (9\text{-}5)$$

$\Delta H_{25^\circ} = +3.5$ kcal $\qquad \Delta F_{25^\circ} = +16$ kcal

Physical Properties of Orthophosphoric Acid

In crystalline form, orthophosphoric acid is known as the anhydrous acid, H_3PO_4 (m.p. = 42.35°C.), and the hemihydrate, $H_3PO_4 \cdot {}^1/_2\ H_2O$ (m.p. = 29.32°C.). A phase diagram[11] of these two compounds is given in Figure 9-1. A report[12] of a decihydrate, $H_3PO_4 \cdot 0.1\ H_2O$, appears to be unfounded.[11,13] Pure H_3PO_4 crystallizes rather slowly, and it is very easy to supercool concentrated orthophosphoric acid to obtain a glass. The glassy transition point[14] for H_3PO_4 is −121°C.

In addition to the data of Figure 9-1, several other phase studies involving orthophosphoric acid have been described in the literature. The solubility of H_3PO_4 in ether[15] and of ether in H_3PO_4 is known,[16] and the partition coefficient for H_3PO_4 between ether and water has been reported.[17]

[9] W. D. Larson, *J. Phys. Colloid Chem.*, **54**, 310 (1950) (undissoc. part of H_3PO_4); R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949) (NaH_2PO_4 and KH_2PO_4); R. G. Bates, *J. Research Natl. Bur. Standards*, **39**, 411 (1947) (KH_2PO_4 plus Na_2HPO_4 in presence of NaBr or NaI); C. M. Mason and W. M. Blum, *J. Am. Chem. Soc.*, **69**, 1246 (1947) (H_3PO_4); K. L. Elmore, C. M. Mason, and J. H. Christensen, *J. Am. Chem. Soc.*, **68**, 2528 (1946) (H_3PO_4); J. M. Stokes, *Trans Faraday Soc.*, **41**, 685 (1945) (NaH_2PO_4 and KH_2PO_4). R. C. Breckenridge, Doctoral Thesis, Massachusetts Institute of Technology, 1942 (H_2O in Na and K phosphates and arsenates); H. W. Robinson, *J. Biol. Chem.*, **82**, 775 (1929) (phosphate buffers), E. J. Cohn, *J. Am. Chem. Soc.*, **49**, 173 (1927) (buffers).

[10] K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).

[11] W. H. Ross and H. M. Jones, *J. Am. Chem. Soc.*, **47**, 2165 (1925).

[12] A. Smith and A. W. C. Menzies, *J. Am. Chem. Soc.*, **31**, 1183 (1910).

[13] H. Giran, *Compt. rend.*, **146**, 1270 (1908).

[14] P. P. Kobeko, E. V. Kuvshinskii, and N. I. Shishkin, *J. Phys. Chem. (U.S.S.R.)*, **9**, 387 (1937).

[15] M. Rabinowitsch and S. Jakubsohn, *Z. anorg. u. allgem. Chem.*, **129**, 55 (1923).

[16] C. Marie and G. Lejune, *Monatsh.*, **53-54**, 69 (1929).

[17] M. Bachelet, E. Cheylan, and J. Le Bris, *J. chim. phys.*, **44**, 302 (1947).

Freezing point data on systems of H_3PO_4 with fifteen different organic compounds are available,[18] and mixtures of H_3PO_4 and HNO_3 have also been studied by several authors.[19]

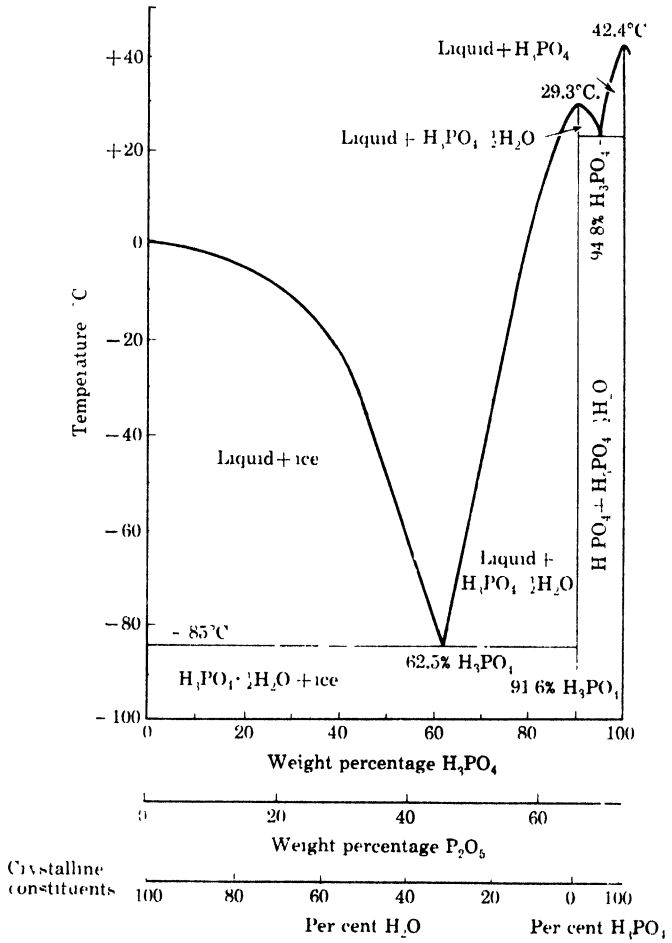


Fig. 9-1. Phase diagram of the system H_2O–H_3PO_4

[18] G. B. King and J. H. Walton, *J. Phys. Chem.*, **35**, 1745 (1931), also see I. L. Krupatkin, *Zhur. Obscheĭ Khim.*, **22**, 184 (1952) or *J. Gen. Chem. U.S.S.R.*, **22**, 229 (1952) for the system H_3PO_4-phenol.

[19] E. E. Babkin, *J. Chem. Ind. (U.S.S.R.)*, **14**, 99 (1937), E. Berl, K. Andress, and E. Escales, *Beitr. Kenntnis Mischsäure*, **1937**, 55 pp., G. Jander and H. Wendt, *Z. anorg. Chem.*, **257**, 26 (1948).

The boiling point, density,[20] heat capacity, refractive index, and electrical conductivity of orthophosphoric acid solutions of various concentrations are presented in Table 9-1.[20–22] The viscosity,[22] and vapor pressure[21,23] of phosphoric acid solutions are given as functions of temperature in Tables 9-2 and 9-3, respectively.

TABLE 9-1
Physical Properties of Aqueous Solutions of Phosphoric Acid

Concentration		Density					Electrical conductivity at 18°C.	
Per cent H_3PO_4	Per cent P_2O_5	$d_{25°}$ (g./ml.)	$-d(d)/dt$	B.p (°C.)	$n_D^{17.5}$	Sp. heat (cal./g.)[a]	Specific, K (mhos)	Equivalent, Λ (mhos)
0	0	0.9971		100.0	1.33320			113
5	3.62	1.0241	0.00029	100.1	1.33775	0.973		
10	7.24	1.0523	0.00034	100.2	1.34203	0.939	0.0566	17.6
20	14.49	1.1129	0.00038	100.8	1.35032	0.871	0.1129	16.6
30	21.73	1.1794	0.00045	101.8	1.35846	0.798	0.1654	15.3
50	36.22	1.3334	0.00059	108		0.656	0.2073	10.2
75	54.32	1.5725	0.00073	135		0.542	0.1209	3.65
85	61.57	1.6850	0.00078	158		0.493	0.0780	1.78
100	72.43	1.8741	0.00084	261				
115	83.29	2.044	0.0009					

[a] Average value from 20 to 120°C.

When the heat of vaporization of water from orthophosphoric acid is calculated from vapor pressure data, such as are shown in Table 9-3, it is found that the value of the heat remains low until, at about 96 wt.-% H_3PO_4, it starts to rise very sharply and uniformly with composition. This indicates that there is a change in composition of the acid in the neighborhood of 96% H_3PO_4—a conclusion that is discussed further in a following section of this chapter.

[20] J. H. Christiansen and R. B. Reed, *Ind. Eng. Chem.*, **47**, 1277 (1955), E. P. Egan and B. B. Luff, *ibid.*, **47**, 1280 (1955).

[21] T. D. Farr, *Tennessee Valley Authority Chem. Eng. Rept. No 8*, "Phosphorus-Properties of the Element and Some of Its Compounds," Wilson Dam, Ala., 1950.

[22] *Monsanto Chemical Co. Tech. Bull. No P-26*, "Phosphoric Acid, Its Physical and Chemical Properties," St. Louis, Mo., 1946, also see S. I. Sklyarenko and I. V. Smirnov, *J. Phys. Chem. (U.S.S.R.)*, **25**, 24 (1951).

[23] B. J. Fontana, *J. Am. Chem. Soc.*, **73**, 3348 (1951).

TABLE 9-2
Approximate Viscosity of Phosphoric Acid Solutions
(Centipoises)

Concentration (% H_3PO_4)	Temperature (°C.)							
	20°	30°	40°	60°	80°	100°	140°	180°
0	1 0	0 80	0 66	0 47	0 36	0 28	0 19	0.14
5	1 1	0 91	0 75	0 55	0 42	0 33	0 22	0 15
10	1 3	1 0	0 87	0 63	0 48	0 38	0 26	0 18
20	1 8	1 4	1 2	0 86	0.65	0 52	0 34	0.24
30	2 6	2 0	1 6	1 2	0 91	0 72	0 49	0.37
50	5 7	4 4	3 4	2 4	1.8	1 4	1 0	0 82
75	24	16	12	7 4	5 1	3 8	2.4	1.8
85	47	32	23	13	8 4	5 8	3 5	2 4
100	263	151	99	46	26	17	8 1	4 7
115	2300	1100	570	195	93	55	21	9 8

TABLE 9-3
Vapor Pressure of Water over Phosphoric Acid Solutions

Concentration (wt % H_3PO_4)	Vapor pressure (mm Hg) at temperature (°C.)				
	25	40	60	80	100
0 0	23 76	55 32	149 4	355 1	760 0
5 00	23 47	54 6	148	349	745
10 00	23 16	54 0	145	345	736
20 00	22 40	52 2	141	335	713
30 00	21 27	49.6	135	320	683
50 00	16.68	39 4	108	262	567
65.00	10.66	25.4	71.5	176	388
85.00	2.24	5 7	15.5	46 5	108
101.1	0.022	0.069	0 266	0 883	2 58
109 9	$5\ 1 \times 10^{-6}$	$2\ 7 \times 10^{-5}$	2×10^{-4}	$1\ 1 \times 10^{-3}$	$5\ 4 \times 10^{-3}$

Brief Chemistry of Orthophosphoric Acid

All pure orthophosphoric acid made today is manufactured from elemental phosphorus according to the following equations.

$$P_4 + 5\ O_2 \longrightarrow P_4O_{10} \qquad (9\text{-}6)$$

$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4$$

The oxidation of the liquid white phosphorus is carried out by using several volumes of air in excess of that demanded by equation 9-6, with part of this

air being introduced into the nozzles which atomize the phosphorus. In some cases, the resulting phosphorus pentoxide is collected, but it is usually hydrated in the equipment in which the phosphorus is burned. Commercial 75–85% orthophosphoric acid is very pure, containing no more than a few parts per million of the lower oxyacids of phosphorus The major impurity, arsenic, is removed from the acid by adding sulfide and filtering.

Aside from its acid behavior in forming salts and esters, phosphoric acid is quite inactive at normal temperatures. Thus, it is sometimes used as a substitute for sulfuric acid when the oxidizing properties of the latter are not wanted. The reduction of phosphoric acid by strong reducing agents, such as hydrogen or carbon, does not occur at a measurable rate at temperatures below 350 400°C. At elevated temperatures, phosphoric acid is fairly reactive toward most metals and their oxides, attacking such refractory oxides as quartz. Usually the reaction products resulting from the attack of phosphoric acid on refractory oxides is a sludge consisting of colloidal crystalline or amorphous orthophosphates which are sometimes contaminated with amorphous salts of the condensed phosphoric acids when the temperature is sufficiently high.

When phosphoric acid reacts with metal surfaces, the surface often becomes covered with a phosphate coating This effect has been commercialized in "phosphatization" processes for putting protective and paint-adherent coatings on metals, such as iron, aluminum, and zinc. In the phosphatization of iron, the metal surface is treated with a solution of phosphoric acid containing zinc, iron, or manganese plus occasional small amounts of materials affecting redox potentials and oxidation rates. Examination of these phosphatic coatings indicates that they consist primarily of tertiary phosphates of iron, zinc, or manganese. Although phosphatizing has been known and practiced for about 40 years in the United States and England, several recent, relatively comprehensive reviews of the theoretical basis of this process have been written in German.[24]

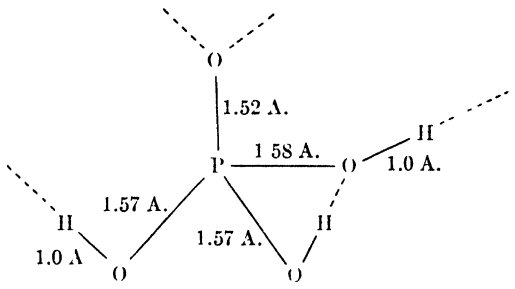
Structure of Orthophosphoric Acid

X-ray diffraction structure studies have been carried out on both crystalline anhydrous orthophosphoric acid and its hemihydrate.[25] In both cases, four formula weights were found per unit cell of the crystals which

[24] A. Wustefeld, *Arch. Metallkunde*, **3**, No. 1, 43 (1949); *ibid.*, **3**, No 7, 253 (1949), W. Machu, *Metallwirtschaft*, **22**, No. 33-35, 481 (1943), R Justh, *Korrosion u. Metallschutz*, **12**, 202 (1936).

[25] S. Furberg, *Acta Chem. Scand.*, **9**, 1557 (1955); J P Smith, W E. Brown, and J. R. Lehr, *J. Am Chem. Soc.*, **77**, 2728 (1955)

belong to the monoclinic system. In the anhydrous acid, three of the oxygen atoms of the PO_4 group (shown below) are bonded to hydrogen atoms which form hydrogen bonds to oxygens of other PO_4 groups. As might be expected, the P-O distance to the "isolated oxygen" (which, of course, has hydrogen bonds) is shorter and hence has somewhat more π-character than the P-O distances to the hydroxyl oxygens.



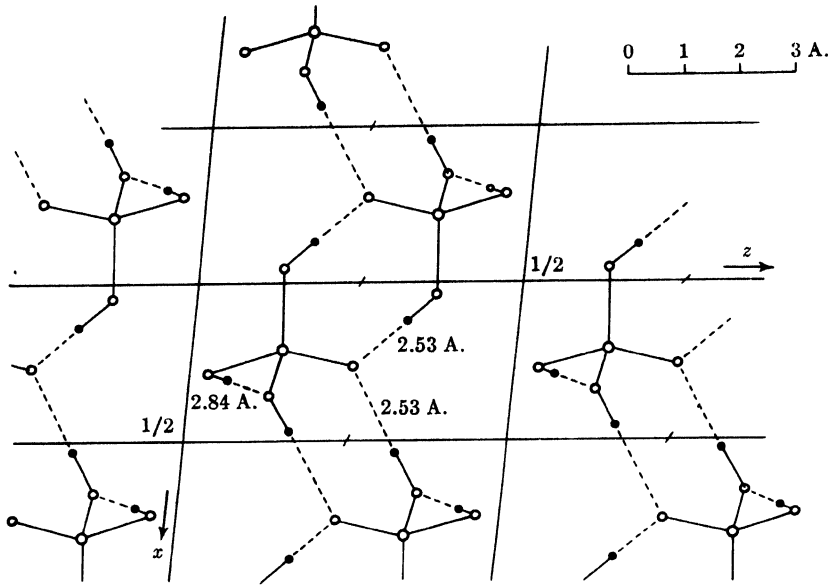
(9-7)

In this crystal the PO_4 groups exhibit trigonal symmetry in that the three HO—P—OH bond angles are found to be equal (105–106°) and smaller than the three HO—P—$O_{isolated}$ angles which equal 112°, within experimental error. The bond between the phosphorus and the isolated oxygen atom is thus the axis of symmetry of the PO_4 group. The electron density maps calculated by Furberg[25] show that the phosphorus and oxygen atoms share electrons, and that little or no loss of electrons from the phosphorus to the oxygen takes place.

The hydrogen bonds in the crystal hold the PO_4 groups together into sheets parallel to the (001) plane. This is shown below in a projection down the *b* axis of the crystal. The internuclear distances between the hydrogen-bonded oxygen atoms are given.

An x-ray structure study has also been carried out on liquid phosphoric acid.[26] Radial distribution curves, which resemble quite closely those of aqueous solutions of sulfuric acid, indicate that the phosphate ions consist of tetrahedral PO_4 groups. In a solution containing 86% H_3PO_4, the phosphate ions are interconnected by hydrogen bonds, with the O-H-O distance being 2.85 A. if the P-O distance is taken as 1.56 A. Most of the time there is a single hydrogen bond between any two PO_4 ions, but there

[26] O Bastiansen and C. Finbak, *Tidskr. Kjemi, Bergvesen Met.*, **4**, 40 (1944); *Arch Math. Naturvidenskab*, **B47**, No 12, 1 (1944), C. Finbak, *Tidskr. Kjemi, Bergvesen Met*, **3**, 40 (1943).



(9-8)

are indications that double and triple hydrogen bonds occur to a lesser extent. In a more dilute solution (54% H_3PO_4), the phosphate ions are hydrogen bonded to the water liquid lattice, rather than to other phosphate ions. The O-O distance corresponding to packing of PO_4 ions which are not held together by hydrogen bonds is about 3.2 A. The radial distribution curves on which these interatomic distances are based were corrected for x-ray absorption to decrease systematic errors which would otherwise cause pronounced deviations.

The structure of liquid orthophosphoric acid has also been studied by Raman spectroscopy.[27,28] Orthophosphoric acid, as well as its alkali metal salts, exhibits a characteristic Raman pattern of four lines. The frequencies of these four lines are changed very little when going from 100% H_3PO_4 to 10% H_3PO_4. The four observed frequencies correspond to a totally

[27] A. Simon and M. Weist, *Z. anorg. u. allgem. Chem.*, **268**, 301 (1952); *Wiss. Z. Tech. Hochschule Dresden*, **1**, 293 (1951/52); A. Simon and G. Schulze, *Z. anorg. u. allgem. Chem.*, **242**, 313 (1939).

[28] T. J. Hanwick and P. O. Hoffmann, *J. Chem. Phys.*, **19**, 708 (1951); *ibid.*, **17**, 1166 (1949); J. P. Mathieu and J. Joques, *Compt. rend.*, **215**, 346 (1942); C. S. Venkateswaran, *Proc. Indian Acad. Sci.*, **3A**, 25 (1936); Takeshi Taketa, *J. Sci. Hiroshima Univ.*, **15**, 139, 151 (1953).

symmetrical vibration (species A_1) occurring at about 900 cm.$^{-1}$, a doubly degenerate vibration (species E) at about 360–420 cm.$^{-1}$, and two triply degenerate vibrations (species F_2) at about 1050 cm.$^{-1}$ and at about 500 cm.$^{-1}$. This spectrum is consistent with a five-atom molecule, XY_4, of tetrahedral symmetry, T_2. It should be noted that the spectrum of concentrated orthophosphoric acid does not exhibit the band belonging to the hydroxyl group, which is usually found in concentrated oxyacids such as H_2SO_4. (Some organic acids, *e.g.*, formic and acetic acids, also do not show the hydroxyl band.) However, substitution of deuterium for hydrogen causes a decrease in frequency which indicates that there is some participation of the hydrogen or deuterium atoms in the vibrations of the PO_4 group. These results have been explained by Simon and coworkers[27] as being due to hydrogen bonds holding neighboring PO_4 ions together into a macromolecular structure in the case of the concentrated acids. In the case of dilute acids, the entire liquid is still held together by hydrogen bonding; but, as would naturally be expected, the water molecules are involved in the macrostructure. This explanation is in accord with the fact that the spectrum of phosphoric acid remains unchanged on the addition of other mineral acids (with the exception of perchloric acid), and it is also in agreement with spectral measurements on orthophosphoryl halides and the esters of orthophosphoric acid.

The over-all picture of liquid phosphoric acids derived from these various studies is that the liquid is bound together by a complicated hydrogen bridge system.[29] An experiment on exchange of heavy oxygen between water and tripotassium phosphate in solution shows that at least three and probably all four of the oxygen atoms of the PO_4 group can exchange with water.[30] Presumably, this means that the water molecules are involved in the proton-exchange process of the orthophosphate ions, so that there is also an occasional exchange of oxygen atoms between the PO_4 ions and the water. This hydrogen-bridge concept is consistent with the low diffusion coefficient[31] of phosphoric acid ($k_{20°} = 0.692$ for 1 N H_3PO_4 as compared to $k_{20°} = 1.350$ for 1 N H_2SO_4). The electrical conductivity of orthophosphoric acid is also in accord with this picture.

Assay[32] by paper chromatography of increasingly concentrated phosphoric acids shows that the pyrophosphate ion appears in the acid when the

[29] K. Wirtz, *Z. Elektrochem.*, **54**, 47 (1950).

[30] E. Blumenthal and J. B. M. Herbert, *Faraday Soc.*, **33**, 849 (1937).

[31] I. W. Oholm, *Finska Kemistsamfundets Medd.*, **30**, 69 (1921); also see H. Brintzinger and Ch. Ratanarat, *Z. anorg. u. allgem. Chem.*, **228**, 64 (1936); *ibid.*, **222**, 317 (1935) for data on dialysis of the phosphate ion.

[32] A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).

H_2O/P_2O_5 mole ratio is still greater than three—the value corresponding to 100% H_3PO_4. This means that the presence of $H_4P_2O_7$ must be counterbalanced by some free water, as shown by the following equation

$$2\ H_3PO_4 \rightleftharpoons H_4P_2O_7 + H_2O \qquad (9\text{-}9)$$

The equilibrium constant (based on mole fractions) for equation 9-9 is approximately 4×10^{-3}, although neglect of activities causes this constant

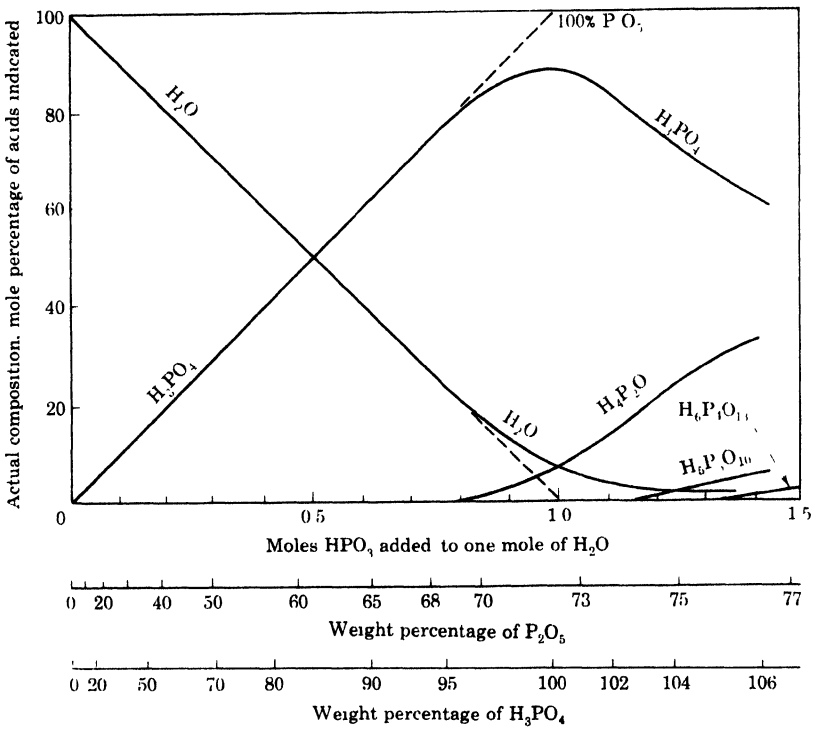


Fig. 9-2. Actual molecular composition of equilibrium liquid phosphoric acids[32] containing from 0 to 77% P_2O_5, as plotted on an arbitary scale of HPO_3/H_2O

to vary somewhat. Experimentally,[32] it is found that 12.7% of the total P_2O_5 in 100% liquid H_3PO_4 is present in the form of pyrophosphoric acid. When crystallization of 100% H_3PO_4 takes place, equation 9-9 shifts quite completely to the left. On the other hand, when pure crystals of H_3PO_4 are melted, the equilibrium of equation 9-9 will then come into effect. A plot of the mole percentages of the various constituents present in phosphoric

acid ranging in concentration from 0 107% H_3PO_4 is given in Figure 9-2. As is apparent from this figure, the concentration of pyrophosphoric acid becomes essentially nil only below 95% H_3PO_4 (according to the equilibrium constant for equation 9-9, about 2% of the total P_2O_5 would be present as the pyrophosphate ion in 95% H_3PO_4).

According to Simon,[27] when anhydrous crystalline orthophosphoric acid is dissolved in ethyl acetate (25% soln of H_3PO_4 in $CH_3COOC_2H_5$), there is no formation of pyrophosphoric acid as indicated by equation 9-9 This is considered by Simon as a proof that the formation of free water and pyrophosphoric acid is primarily due to interactions within the hydrogen-bonded network structure However, it should be noted that sulfuric and nitric acids, in which the network structure is less pronounced than in phosphoric acid, also show some formation of free water in the concentration range near 100% acid.[33] This partial dehydration in concentrated oxyacids is probably attributable to the fact that there is a great amount of covalent bonding of the hydrogen by the oxygen atoms in the concentrated acids—bonding having about the same free energy of formation as the O—H bonds in water—so that a reorganization process leading to some condensation (see Chapt. 12) is energetically possible The existence of strong interactions in concentrated phosphoric acids (> 95% H_3PO_4) shows up, as previously noted, in the heat of vaporization of these acids and in their high viscosities and activation energies for flow.

ALKALI METAL PHOSPHATES

Phase Equilibria for Alkali Orthophosphate Solutions

The phase equilibria of lithium sodium, potassium, and ammonium orthophosphates in water have been the subject of a recent review by Wendrow and Kobe.[34] The conclusions of these authors are reported below:

The lithium system is very different from that of the orthophosphates of the other alkali metals. The lithium system is characterized by the insolubility of trilithium orthophosphate and the absence of the dilithium salt from the phase diagram. Also, neither of the lithium orthophosphates is hydrated. The little information[35] available on the lithium orthophosphate system is presented in Figure 9-3, in which the composition is plotted against two orthogonal coordinates—the weight percentage of Li_2O and the

[33] R. J. Gillespie, E. D Hughes, and C K Ingold, *J. Chem. Soc.*, **1950**, 2473; *ibid.*, **1950**, 2552.

[34] B Wendrow and K A. Kobe, *Chem Revs.*, **54**, 891 (1954)

[35] A. P Rollet and R. Lauffenburger, *Bull. soc chim.*, **1**, 146 (1934)

weight percentage of P_2O_5. The third variable, the weight percentage of H_2O, is then obtained by subtracting the sum of these two values (Li_2O + P_2O_5) from 100. It should be noted that all compositions having a given LiO_2/P_2O_5 ratio must lie on the same straight line passing through the origin. In this phase diagram, tie lines connect the appropriate portion of the solubility curve with the point representing the composition of the solid phase with which the solution is in equilibrium. The single-phase regions are (1) the area beneath the solubility curve, where an homogeneous solution exists, and (2) the solid crystalline compounds, not shown in the diagram. The areas covered by the tie lines correspond to two-phase regions

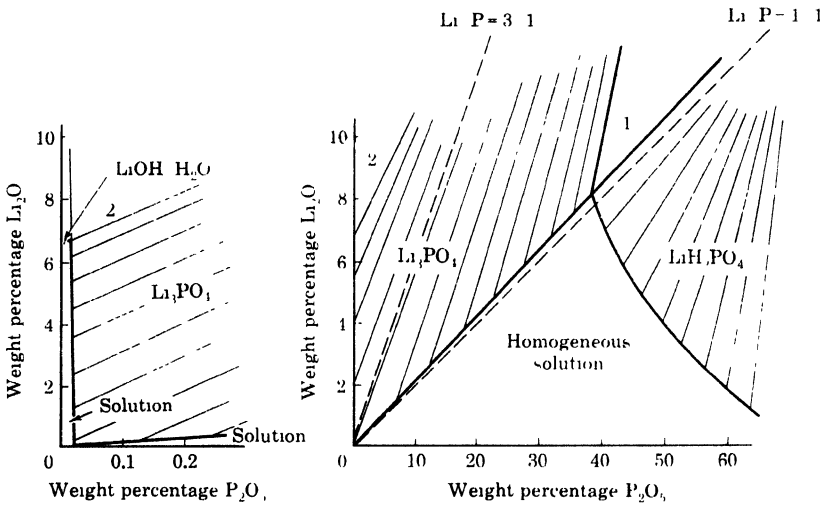


Fig. 9-3 The system Li_2O H_2O–P_2O_5 for the lithium orthophosphate at 0°C

existing between the solubility curve and the equilibrium solid phase. The three-phase regions in the diagram are numbered. Thus, in region 1, the phases are liquid, crystalline Li_3PO_4, and crystalline LiH_2PO_4; in region 2, liquid, crystalline $LiOH \cdot H_2O$, and crystalline Li_3PO_4.

The first phase diagram of the sodium orthophosphates was developed by D'Ans and Schreiner,[36] but their original work has been considerably modified by a number of other authors,[37,38] especially Wendrow and Kobe.[39]

[36] J. D'Ans and O. Schreiner, *Z. phys. Chem.*, **75**, 101, 102 (1910)
[37] H. Menzel and E. von Sahr, *Z. Elektrochem.*, **43**, 104 (1937).
[38] O. T. Quimby, *Chem. Revs.*, **40**, 147 (1947)
[39] B. Wendrow and K. A. Kobe, *Ind. Eng. Chem.*, **44**, 1439 (1952).

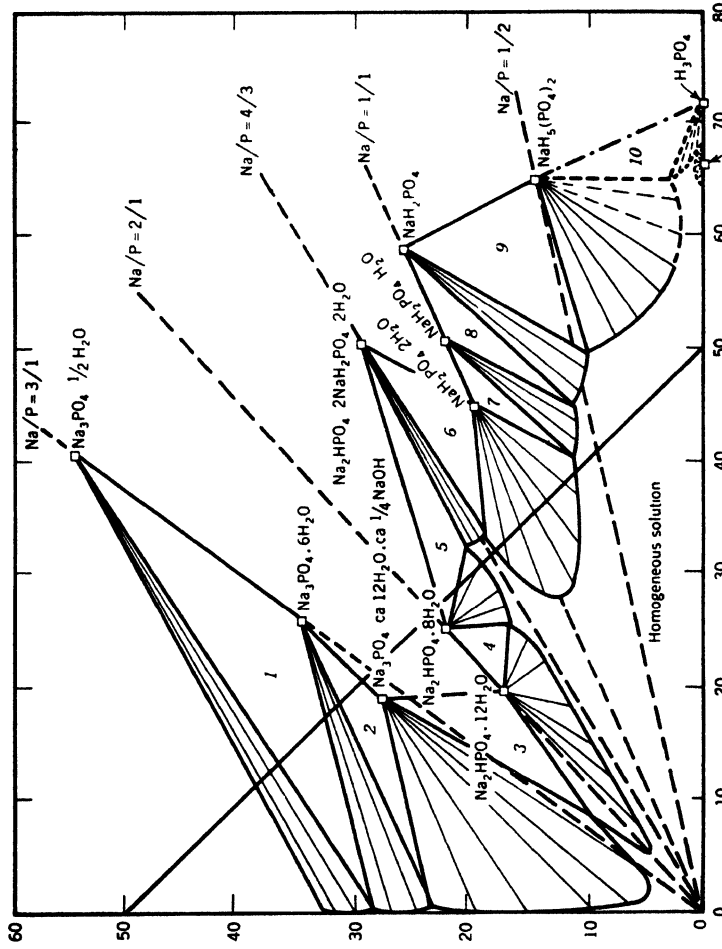


Fig 9-4. The system Na_2O–H_2O–P_2O_5 for the sodium orthophosphates at 25°C. The squares represent crystalline solids. The areas covered by tie lines are two-phase areas, whereas the three-phase areas are numbered

The 25°C. isotherm, resulting from the work of all of these investigators is shown in Figure 9-4, which is plotted in the same manner as the lithium orthophosphate phase diagram. However, in the sodium orthophosphate diagram there are twelve solid phases (denoted by squares) and ten three-phase areas (numbered) at 25°C.

It should be noted that the so-called "dodecahydrate" of trisodium phosphate, which is shown as $Na_3PO_4 \cdot ca.12\ H_2O \cdot ca.{}^1/_4\ NaOH$, does not lie on

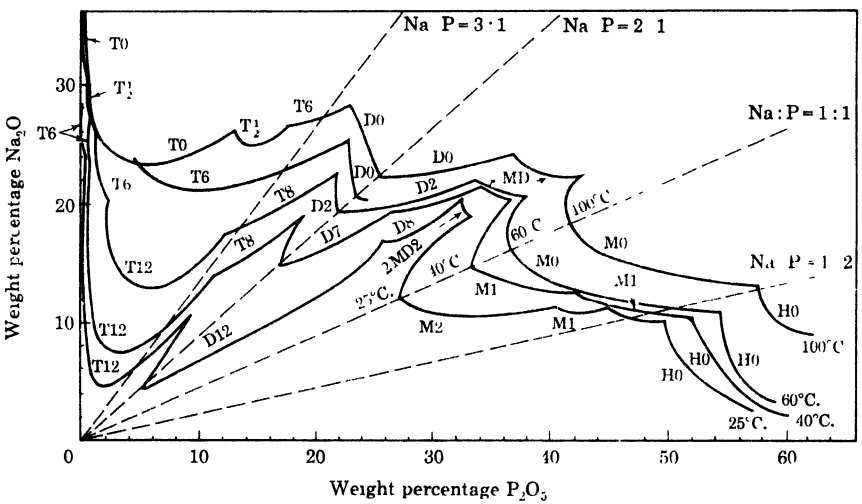


Fig. 9-5. Solubility curves at different temperatures in the Na_2O–H_2O–P_2O_5 orthophosphate system. The various crystalline salts shown above are T0 = Na_3PO_4, T1/2 = $Na_3PO_4\ {}^1/_2H_2O$; T6 = $Na_3PO_4\ 6H_2O$, T8 = $Na_3PO_4\ 8H_2O$; T12 = Na_3PO_4 ca $12H_2O$ - ca.$^1/_4NaOH$; D0 = Na_2HPO_4, D2 = $Na_2HPO_4\ 2H_2O$, D7 = $Na_2HPO_4\ 7H_2O$, D8 = $Na_2HPO_4 \cdot 8H_2O$, D12 = $Na_2HPO_4 \cdot 12H_2O$; M0 = NaH_2PO_4; M1 = $NaH_2PO_4 \cdot H_2O$, M2 = $NaH_2PO_4\ 2H_2O$, and H0 = $NaH_5(PO_4)_2$

the line corresponding to Na/P = 3/1. This means that the "dodecahydrate" is not a simple hydrate but contains excess sodium hydroxide. The problem of the composition of this salt is one that has been studied carefully.[40] According to one school of thought on the matter,[38] there is a limited solid solution between the three components Na_3PO_4, H_2O, and NaOH. This conclusion is based on the fact that the various "dodecahy-

[40] R. N. Bell, *Ind. Eng. Chem.*, **41**, 2901 (1949); K. A. Kobe and A. Leipper, *ibid.* **32**, 198 (1940); also see ref. 34 and, for 2 $Na_3PO_4 \cdot NaF \cdot 19H_2O$, see E. W. Neuman, *Z. Krist.*, **86**, 298 (1933).

drates" which have been prepared exhibit the same microscopic appearance and essentially the same x-ray diffraction pattern, even though the composition is variable. The most recent work,[34,39] however, has been interpreted in accord with the idea that there are two limiting, isomorphous alkaline mixed salts of trisodium phosphate dodecahydrate represented by the formulas $Na_3PO_4 \cdot {}^1/_7\, NaOH \cdot 12\, H_2O$ and $Na_3PO_4 \cdot {}^1/_4\, NaOH \cdot 12\, H_2O$.

There are a number of mixed salts closely related to the "dodecahydrate" of trisodium phosphate.[40] Examples are $Na_3PO_4 \cdot ({}^1/_4\text{–}{}^1/_7)\, NaNO_2 \cdot 11$

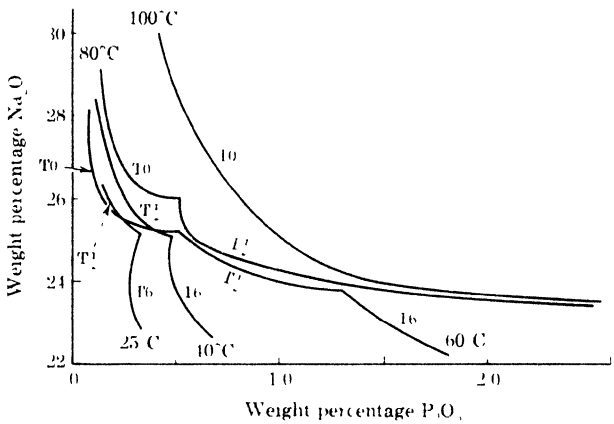


Fig. 9-6. The alkaline region of the Na_2O–H_2O–P_2O_5 phase diagram for sodium orthophosphates. The symbols are the same as the ones used in Figure 9-5.

H_2O, $Na_3PO_4 \cdot ({}^1/_5\text{–}{}^1/_7)\, NaMnO_4 \cdot 11\, H_2O$, $Na_3PO_4 \cdot {}^1/_4\, NaOCl \cdot 11\, H_2O$, $Na_3PO_4 \cdot {}^1/_5\, NaCl \cdot 11\, H_2O$, and $Na_3PO_4 \cdot {}^1/_4\, NaNO_3 \cdot 11\, H_2O$. Other similar salts are $Na_3PO_4 \cdot NaBO_2 \cdot 18\, H_2O$ and $2\, Na_3PO_4 \cdot NaF \cdot 19\, H_2O$.

The temperature dependence of the solubilities represented in this phase diagram is shown in Figure 9-5. To avoid undue complication of this figure, only the solubility curves themselves are shown. It should be noted that two double salts between the monosodium and the disodium phosphate are formed. At low temperatures, there is the salt $Na_4H_5(PO_4)_3 \cdot 2\, H_2O$ (equivalent to $Na_2HPO_4 \cdot 2\, NaH_2PO_4 \cdot 2\, H_2O$). This salt is found at 25 and 40°C. At higher temperatures in solutions exhibiting essentially the same Na_2O/P_2O_5 ratio, the salt $Na_3H_3(PO_4)_2$ (anhydrous $Na_2HPO_4 \cdot NaH_2PO_4$) is found. This salt is the saturating phase at 60 and 100°C.

The highly alkaline region of Figure 9-5 is plotted on an expanded scale in Figure 9-6. It should be noted that, in this region, there is a consider-

able difference between the 100°C. isotherm and the isotherms at lower temperatures. At 100°C., anhydrous Na_3PO_4 is the saturating phase over a large concentration range, whereas at lower temperatures it covers a considerably shorter region of solution composition.

The phase diagram for the potassium orthophosphate system is shown in Figure 9-7. This system differs from the sodium system primarily in the

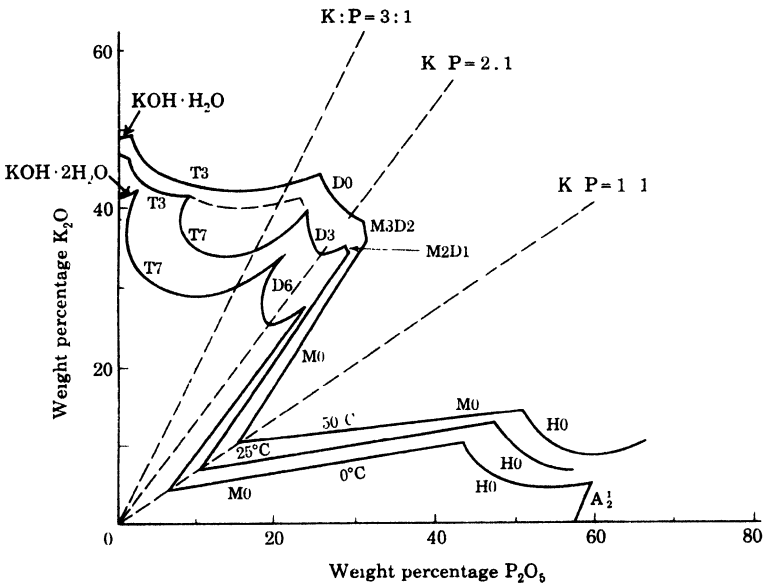


Fig. 9-7. Solubility curves for the system K_2O-H_2O-P_2O_5 for potassium orthophosphate at various temperatures The various crystalline salts are T3 = $K_3PO_4 \cdot 3H_2O$, T7 = K_4PO_4 $7H_2O$, D0 = K_2HPO_4; D3 = $K_2HPO_4 \cdot 3H_2O$; D6 = $K_2HPO_4 \cdot 6H_2O$, M3D2 = $K_7H_5(PO_4)_4 \cdot 2H_2O$; M2D1 = $K_5H_4(PO_4)_3 \cdot H_2O$, M0 = KH_2PO_4; H0 = $KH_5(PO_4)_2$, $A^1/_2$ = $H_3PO_4 \cdot {}^1/_2H_2O$

high solubility of the more alkaline potassium orthophosphates. The first branch of the isotherms in the highly alkaline region has as its equilibrium solid phase hydrated potassium hydroxide which exists only over a short range of concentration. This, too, is different from the sodium system, in which the hydroxide has not been established in the phase diagram. The isotherms of the potassium system are based on the work of a number of

authors,[36,37,41,42] especially the studies of Berg and of Ravich.[42] The 25°C. isotherm is interesting in that two branches of the curve are found near the K_2O/P_2O_5 ratio of 3. The solubility of $K_3PO_4 \cdot 3\ H_2O$ can readily be studied as a metastable phase over the region where the proper saturating phase is $K_3PO_4 \cdot 7\ H_2O$. The 50°C. isotherm may contain several hydrated double salts between K_2HPO_4 and KH_2PO_4. However, there are only sufficient data on one of them, $K_7H_5(PO_4)_4 \cdot 2\ H_2O$ (equivalent to

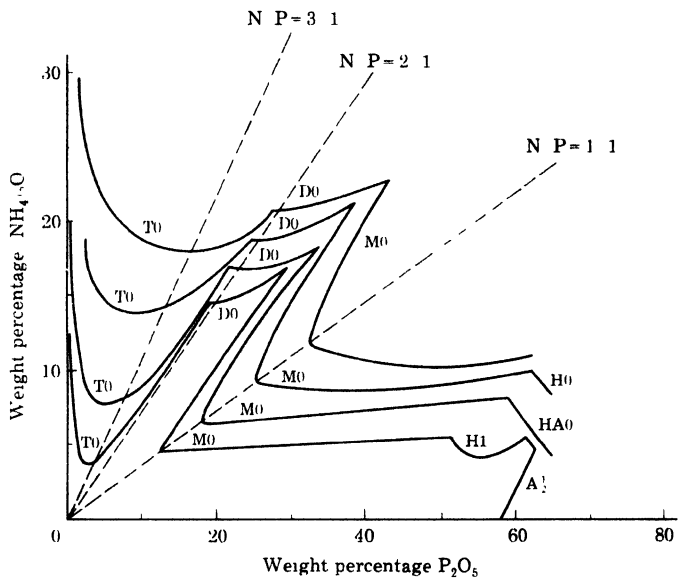


Fig. 9-8 Solubility curves in the system NH_3–H_2O–P_2O_5 for ammonium orthophosphates The various crystalline salts are T0 = $(NH_4)_3PO_4$; D0 = $(NH_4)_2HPO_4$; M0 = $NH_4H_2PO_4$; H0 = $NH_4H_5(PO_4)_2$; HA0 = $NH_4H_8(PO_4)_3$; H1 = $NH_4H_5(PO_4)_2 \cdot H_2O$; and $A^1/_2$ = $H_3PO_4 \cdot {}^1/_2H_2O$.

$KH_2PO_4 \cdot 3\ K_2HPO_4 \cdot 2\ H_2O$) to show that it is a stable phase at 50° C. This is the only one shown on the 50°C. isotherm. The double salt, $K_5H_4(PO_4)_3 \cdot H_2O$ (equivalent to $KH_2PO_4 \cdot 2\ K_2HPO_4 \cdot H_2O$), which appears to be a saturating phase on the 25°C. isotherm, can be obtained only in a metastable

[41] E. G. Parker, *J. Phys. Chem.*, **18**, 653 (1914); E. Jänecke, *Z. phys. Chem.*, **127**, 71 (1927).

[42] L. G. Berg, *Bull. acad. sci. U.R.S.S.; Classe sci. math. nat., Ser. chim.*, **1938**, No. 1, 161; M. I. Ravich and N. V. Troitskaya, *Kalii* (*U.S.S.R.*), **1937**, No. 3, 34; and M. I. Ravich, *ibid.*, **1936**, No. 10, 33.

condition by crystallization at 50°C. Two other double salts are believed to occur in the system. These are the metastable $K_3H_3(PO_4)_2 \cdot 2\ H_2O$ = $KH_2PO_4 \cdot K_2HPO_4 \cdot 2\ H_2O$ and a salt of somewhat uncertain composition, $K_7H_{11}(PO_4)_6 \cdot x\ H_2O$ = $5\ KH_2PO_4 \cdot K_2HPO_4 \cdot x\ H_2O$. The exact analysis of these double salts, and especially their water content, is still somewhat problematical. Crystallization of salts which are *not* the stable phases under the conditions of crystallization is a reasonably common occurrence in the potassium orthophosphate system.

Various systems involving ammonium orthophosphates have been extensively studied because of their interest to fertilizer technology. In the simple ammonium orthophosphate–water system,[36,41,43] most of the work on the phase relationships has been carried out at 25°C. However, there has also been some investigation at 0, 50, 60, and 75°C. The data are plotted in Figure 9-8. It should be noted that there are fewer hydrates and double salts in the ammonium than in the sodium or potassium orthophosphate systems.

A number of systems involving ammonium orthophosphates in which there are more components than just $(NH_4)_2O$, H_2O, and P_2O_5 have been studied. Thus, some data[44] are available on the K_2O- $(NH_4)_2O$–H_2O–P_2O_5

[43] B. A. Mouromtzev and L. A. Nazarova, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Sér. chim.*, **1938**, No. 1, 177. B. A. Mouromtzev, *Kalii (U.S.S.R.)*, **1937**, No. 1, 36; J. C. Brosheer and J. F. Anderson, *J. Am. Chem. Soc.*, **68**, 902 (1946); R. Flatt, G. Brunisholz, and S. Chapius-Gottreux, *Helv. Chim. Acta*, **34**, 683 (1951). Also for the ice field see N. S. Kurnakov, M. I. Ravich, and N. V. Troitskaya, *Ann. secteur anal. phys.-chim., Inst. chim. gén. (U.S.S.R.)*, **10**, 275 (1938); and M. I. Ravich and N. V. Troitskaya, *Kalii (U.S.S.R.)*, **1937**, No. 3, 34.

[44] N. K. Voskresenskaya, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshcheĭ Neorg. Khim. Akad. Nauk S.S.S.R.*, **17**, 307 (1949); D. I. Kuznetsov, A. A. Kozhukhovskii, and F. E. Borovaya, *Zhur. Priklad. Khim.*, **21**, 1278 (1948); N. S. Kurnakov, A. Y. Zvorykin, and V. Ya. Ketkovich, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshcheĭ Neorg. Khim. Akad. Nauk S.S.S.R.*, **16**, No. 3, 108 (1948); A. Ya. Zvorykin and V. G. Kuznetsov, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Ser. chim.*, **1938**, No. 1, 195; V. A. Polosin and R. K. Ozolin, *Trudy Tskha, Yubileinyi Sbornik*, **1940**, No. 4, 29; *Kalii (U.S.S.R.)*, **31**, No. 10 (1937); N. S. Dombrovskaya and A. Ya. Zvorykin, *ibid.*, **1937**, No. 2, 24; P. Askenasy and F. Nessler, *Z. anorg. u. allgem. Chem.*, **189**, 305 (1930); E. Jänecke, *Z. physik. Chem.*, **127**, 71 (1927). Also for systems including chloride or nitrate, see N. S. Kunakov, A. Y. Zvorykin, and V. Y. Ketkovich, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshcheĭ Neorg. Khim. Akad. Nauk. S.S.S.R.*, **16**, No. 3, 108 (1948); V. A. Polosin and M. I. Shakhparonov, *J. Phys. Chem. (U.S.S.R.)*, **21**, 119 (1947); *Trudy Tskha, Yubileinyi Sbornik*, **1940**, No. 4, 57; M. I. Ravich and Z. V. Popova, *Ann. secteur anal. phys.-chim., Inst. chim. gen. (U.R.S.S.)*, **14**, 373 (1941); P. F. Bochkarev and A. G. Bergman, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1940**, 379; A. G. Bergman, *Bull. acad. sci. U.R.S.S., Classe math. nat., Ser. chim.*, **1938**, No. 1, 229; A. G. Bergman and P. F. Bochkarev, *ibid.*, **1938**, No. 1, 237; P. F. Bochkarev and A. G. Bergman, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1940**, 379.

system, as well as on the same system containing chloride or nitrate. An unusual region of liquid immiscibility exists in the K_2O-$(NH_4)_2O$-H_2O-P_2O_5 system. This region, consisting of two liquid phases, covers an area from near the K_3PO_4 composition to near NH_3, with this area extending somewhat in the direction of K_2O, in the triangular diagram K_2O-NH_3-P_2O_5. There also appears to be a continuous series of solid solutions between $NH_4H_2PO_4$ and KH_2PO_4 crystals.

Phase studies[45] have also been carried out on the systems[46] $NH_4H_2PO_4$-(NH_4NO_3 or $NaNO_3$) H_2O and the systems[47] $NH_4H_2PO_4$-(NH_4Cl or $NaCl$)-H_2O. Probably the greatest amount of work has been put into the system[48] $(NH_4)_2O$-H_2O SO_3-P_2O_5, since this system is of especial interest in the production of ammonium phosphates from wet-process phosphoric acid containing some H_2SO_4.

Properties of the Alkali Metal Phosphates

One of the most important uses for the alkali metal phosphates is as buffers. One of the best known buffer mixtures involving phosphates is the combination of KH_2PO_4 and Na_2HPO_4. These two salts were chosen because they can be readily purified[49] by recrystallization from water to the

[45] Also see V. P. Blidin, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 887 (1941) for the system: $NH_4H_2PO_4$-NH_2CONH_2-H_2O

[46] S. Ya. Shpunt, *J. Applied Chem.* (*U.S.S.R.*), **19**, 293 (1946); P. F. Bochkarev, *Trudy Vostochno-Sibirskogo Gosudarst. Inst.*, **1937**, No. 3, 3; A. G. Bergman, *Bull. acad. sci. U.R S.S., Classe math. nat, Ser. chim.*, **1938**, No. 1, 229; A. G. Bergman and P. F. Bochkarev, *ibid.*, **1938**, No. 1, 237; *J. Applied Chem.* (*U.S.S.R.*), **10**, 1531 (1937). For addition of NH_4Cl, see A. G. Bergman *et al.*, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshcheĭ Neorg. Khim., Akad. Nauk. S.S.S.R.*, **15**, 157, 200 (1947). Also see S. Ya. Shpunt, *J. Applied Chem.* (*U.S.S.R.*), **13**, 9 (1940); *ibid.*, **20**, 685 (1947) for data on $NH_4H_2PO_4$-$NaNO_3$-H_2O.

[47] N. S. Kurnakov, A. Ya. Zvorykin, and V. Ya. Ketkovich, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshcheĭ Neorg. Khim., Akad. Nauk S.S.S.R.*, **16**, No. 3, 108 (1948); V. A. Polosin, *J. Phys. Chem.* (*U.S.S.R.*), **20**, 1471 (1946); P. Askenasy and F. Nessler *Z. anorg. u. allgem. Chem.*, **189**, 305 (1930). For the systems containing NaCl instead of NH_3Cl, see R. Lauffenburger, *Chimie et industrie*, **45**, No. 3 bis, 188 (1941); R. Lauffenburger and M. Brodsky, *Compt. rend.*, **206**, 1383 (1938).

[48] K. S. Chernova and E. V. Korzh, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 171 (1946); F. V. Bel'chev and A. G. Bergman, *ibid.*, **17**, 520 (1944); S. Uno, *J. Soc. Chem. Ind. Japan*, **43**, 168 (1940); S. I. Vol'fkovich, L. E. Berlin, and B. M. Mantsev, *Trans. Sci. Inst. Fertilizers Insectofungicides* (*U.S.S.R.*), No. **153**, 228 (1940); I. L. Hofman, *Nauch. Inst. Udobreniyam i Insektofungisidam Ya. V. Samoilova*, **1919–39**, 40 (1939); L. E. Berlin and B. M. Mantsev, *J. Applied Chem.* (*U.S.S.R.*), **6**, 385 (1933); S. I. Vol'fkovich, L. E. Berlin, and B. M. Mantsev, *ibid.*, **5**, 1 (1932).

[49] G. G. Manov, *J. Assoc. Offic. Agr. Chemists*, **30**, 500 (1947).

point that an error of less than 0.0002 pH unit is due to residual impurities. The most precise work on this buffer system has been carried out by Bates and Acree[6] on equimolar mixtures of KH_2PO_4 and Na_2HPO_4 for calibrating pH meters in the neutral region. They found that at 25°C. for concentrations ranging from 0.01 to 0.2 molar, the pH of buffers containing equimolar concentrations of each of these two salts is given by the following equation.

$$\text{pH} = 7.169 + 4.78c - 3.287(c)^{1/2} \qquad (9\text{-}10)$$

where c is the total molar concentration of KH_2PO_4 plus Na_2HPO_4.

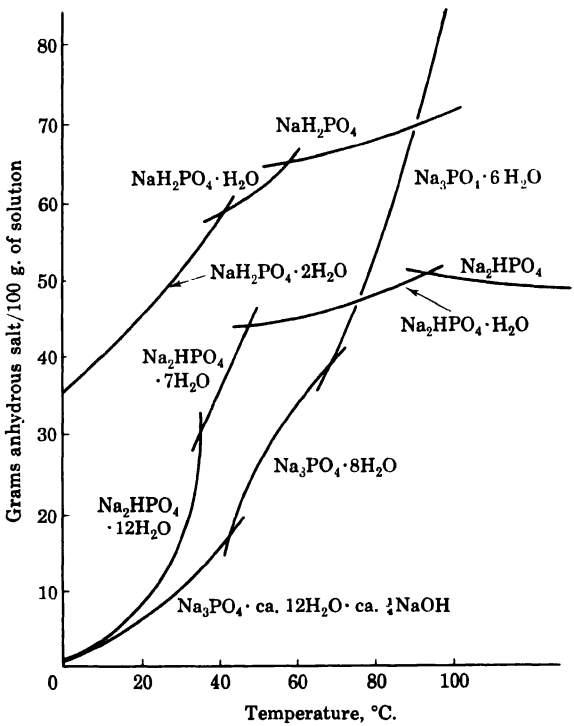


Fig. 9-9. Solubilities of the three common sodium orthophosphates in water.

The solubilities[50] of the common sodium orthophosphates are presented in Figure 9-9. It should be noted that most of the hydrates of these salts

[50] Cited in A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, 3rd ed., D. Van Nostrand Co., Inc., New York, Vol. I, 1940, and Supplement, 1952.

can be in equilibrium with solutions of a different Na_2O/P_2O_5 mole ratio (see Fig. 9-5) at temperatures below the solubility curves given in Figure 9-9. Although the hemihydrate and anhydrous forms of trisodium orthophosphate appear on the phase diagram of Figures 9-5 and 9-6, these compounds do not show up on the solubility curve for trisodium orthophosphate because they dissolve incongruently at any temperature which can be

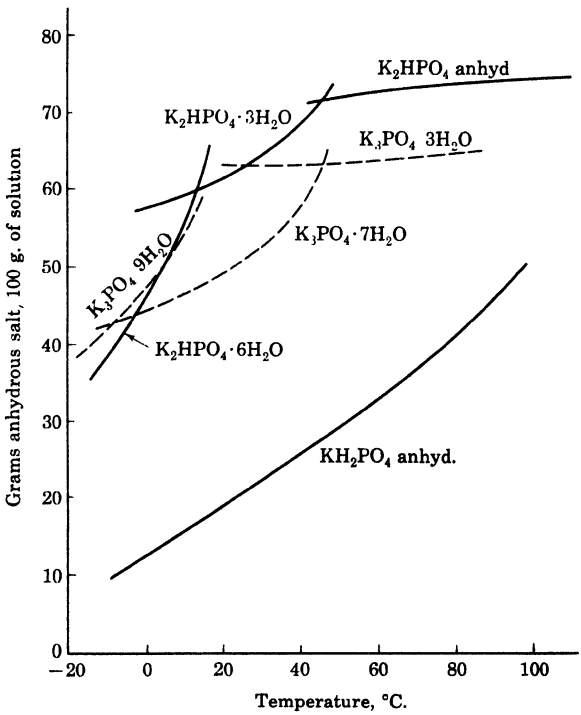


Fig. 9-10. Solubilities of the potassium orthophosphates in water. For a given salt, the hydrate with the lowest solubility is the one which is thermodynamically stable.

achieved at atmospheric pressure. Similarly, hemisodium orthophosphate, $NaH_5(PO_4)_2$, also dissolves incongruently except in a restricted range of temperatures near the boiling point. Only monosodium orthophosphate can be obtained as crystals by cooling or from the initial low-temperature (below 60°C.) dehydration of aqueous solutions of $NaH_5(PO_4)_2$.

In Figure 9-10 the solubilities of the common potassium orthophosphates are given. It should be noted that the di- and tripotassium orthophos-

phates are considerably more soluble than their sodium analogs, but that the hydrates of monosodium orthophosphate are more soluble than the equivalent potassium salt. The solubilities of the common ammonium orthophosphates are given in Figure 9-11.

An interesting phenomenon takes place when ammonia is conducted into a concentrated aqueous solution of tripotassium orthophosphate.[51] First

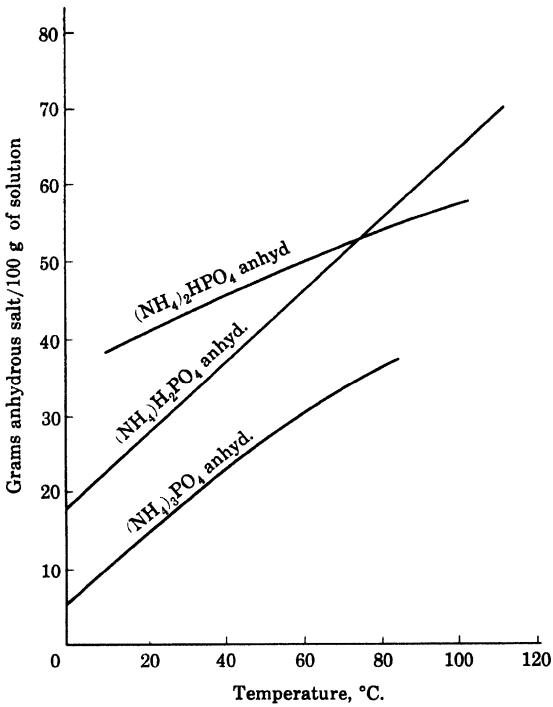


Fig 9-11. Solubilities of the ammonium orthophosphates in water.

the ammonia dissolves and then a second, lighter, ammoniacal layer forms. Finally, the potassium orthophosphate is salted out and the heavier layer thus disappears. When there is an excess of tripotassium orthophosphate, the two-layer liquid system becomes stable in the temperature range from 0 to 60°C. This phenomenon has formed the basis of setting up as many as five liquids in equilibrium with each other.[52] An example of such an equilib-

[51] E. Janecke, *Z. Elektrochem.*, **33**, 518 (1927).

[52] J. F. Carrière, *Chem Weekblad*, **41**, 58 (1945).

rium system is K_3PO_4 soln./NH_3 soln./sodium oleate soln./aniline/hexane. It should be noted that other salts such as K_2CO_3, Rb_2CO_3, or K_3VO_4 can be substituted for the K_3PO_4 in such systems.

In the dry state, the ammonium orthophosphates exhibit a measurable dissociation pressure of ammonia according to the decomposition reactions listed in the following equations. The dissociation pressure[53] of ammonia, in mm. of Hg, over these salts is given by the expression beneath the chemical equation corresponding to the decomposition. T = the absolute temperature.

$$NH_4H_2PO_4(c) \rightleftharpoons NH_3(g) + H_3PO_4(\text{amorph.}) \qquad (9\text{-}11)$$
$$p_{mm} = 0.05 \text{ at } 125°C.$$

$$(NH_4)_2HPO_4(c) \rightleftharpoons NH_3(g) + NH_4H_2PO_4(c) \qquad (9\text{-}12)$$
$$\log p_{mm.} = -3063/T + 1.75 \log T + 3.3$$

$$(NH_4)_5H(PO_4)_2(c) \rightleftharpoons NH_3(g) + 2\,(NH_4)_2HPO_4(c) \qquad (9\text{-}13)$$
$$\log p_{mm.} = -2990/T + 1.75 \log T + 3.3$$

$$(NH_4)_3PO_4(c) \rightleftharpoons NH_3(g) + (NH_4)_2HPO_4(c) \qquad (9\text{-}14)$$
$$\log p_{mm.} = -2503/T + 1.75 \log T + 3.3$$

Ferroelectricity in the Phosphates

About 35 years ago, it was shown[54] that the dielectric behavior of Rochelle salt ($KNaC_4H_4O_6 \cdot H_2O$) was very similar to the magnetic behavior of ferromagnetic materials. Since that time, a number of additional crystals—including some orthophosphates—have been found to exhibit more or less the same anomalous dielectric behavior. These materials are called ferroelectrics[55] or seignette-electric salts. Seignette salt is another name for Rochelle salt, $NaKC_4H_4O_6 \cdot 4\,H_2O$, sodium potassium tartrate. It is named after P. Seignette (1660–1719), who was an apothecary in Rochelle, France. These salts exhibit the following properties which have direct analogs in ferromagnetism:

1. Spontaneous dipole polarization, which is reversible by an external field, appears at a transition from a nonferroelectric to a ferroelectric phase, and this polarization persists over the ferroelectric temperature range. By

[53] A. de Passillé, *Compt. rend.*, **199**, 356 (1934); also see T. E. Warren, *J. Am. Chem Soc.*, **49**, 1904 (1927). For crystallographic data on diammonium phosphate see J. P. Smith, J. R. Lehr, and W. E. Brown, *Acta Cryst.*, **10**, 709 (1957).

[54] J. Valasek, *Phys. Rev.*, **15**, 537 (1920); **17**, 475 (1921); **19**, 478 (1922); **20**, 639 (1922); and **24**, 560 (1924).

[55] For a good review of ferroelectricity in the phosphates see G. Shirane, F. Jona, and R. Pepinsky, *Proc. I. R. E.*, **43**, 1738 (1955).

analogy to ferromagnetism, the transition temperature is called the Curie point.

2. At the Curie point, the dielectric constant rises rather sharply to an abnormally high value (about 10^3), and in most cases the dielectric constant remains high throughout the ferroelectric temperature range. The temperature dependence of the dielectric constant can be described by a Curie-Weiss law as the Curie point is approached in the nonferroelectric phase. In the ferroelectric phase, the dielectric constant shows marked field dependence.

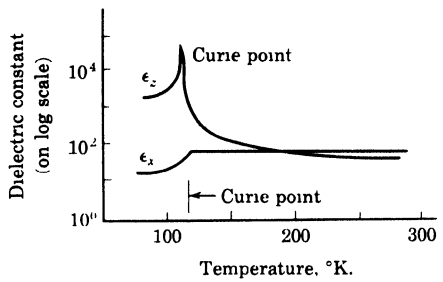


Fig. 9-12. Variation of dielectric constant of KH_2PO_4 with temperature, at 800 cycles/sec. and 200 v./cm.

3. Hysteresis loops are obtained, when the polarization of a crystal in its ferroelectric phase is measured as a function of increasing and decreasing field strength.

4. A crystal in its ferroelectric phase consists of many small spontaneously polarized domains, similar to the domains appearing in ferromagnetic substances.

Although there is a close similarity between ferroelectricity and ferromagnetism, as shown above, it should be remembered that the two are quite different phenomena, and the analogy between the two cannot be pushed too far.

The tetragonal dihydrogen orthophosphates and arsenates of potassium, rubidium, and cesium are ferroelectric crystals.[56] The ammonium dihydro-

[56] G. Busch and P. Scherrer, *Naturwiss.*, **23**, 737 (1935); G. Busch, *Helv. Phys. Acta*, **11**, 269 (1938). P. Baertschi, B. T. Matthias, W. Merz, and P. Scherrer, *Helv. Phys. Acta*, **18**, 240 (1945). F. Seidl, *Tschermaks mineralog. petrog. Mtt.*, **1**, 432 (1950). H. Baumgartner, *Helv. Phys. Acta*, **22**, 400 (1949); **23**, 651 (1950); **24**, 326 (1951); Also see S. Le Montagner, J. Le Bot, and Y. Allain, *Compt. rend.*, **235**, 1199 (1952); **236**, 1409 (1953).

gen orthophosphate, although not ferroelectric, has properties which are very similar.[56] The Curie points of all of these materials are well below room temperature. In Figure 9-12 the change in dielectric constant in the two crystal directions of KH_2PO_4 is shown in the neighborhood of the Curie point. It should be noticed in this figure that the dielectric constant goes as high as 3×10^4 under the conditions of measurement that were used! In Figure 9-13, the effect on polarization of substituting deuterium for hydrogen in the monopotassium orthophosphate is shown.[57] It should be noticed that there is a large positive shift of about 90°C. in the Curie point, resulting from replacing hydrogen with deuterium. A similar positive shift of about 65–70°C. is observed[58] when deuterium replaces

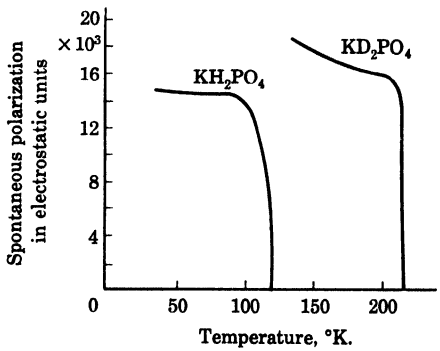


Fig. 9-13. Polarization of monopotassium orthophosphates.

hydrogen in the arsenates (except for the ammonium salt for which the shift is only 23°C.). The Curie point referred to here is the temperature below which the crystal exhibits anomalously high values of the dielectric constant. There are in addition lower temperatures (sometimes called "lower Curie points") at which there are rapid changes in the dielectric properties.

At the upper Curie point there is a large λ-type (order-disorder transition) anomaly in the specific heat.[59] Such transitions have been measured

[57] W. Bantle, *Helv. Phys. Acta*, **15**, 373 (1942).

[58] C. C. Stephenson, J. M. Corbella, and L. A. Russell, *J. Chem. Phys.*, **21**, 1110 (1953). For x-ray data see D. W. Dickson and A. R. Ubbelohde, *Acta Cryst.*, **3**, 6 (1950).

[59] C. C. Stephenson and J. G. Hooley, *J. Am. Chem. Soc.*, **66**, 1397 (1944); J. Mendelssohn and K. Mendelssohn, *Nature*, **144**, 595 (1939) (KH_2PO_4). C. C. Stephenson and A. C. Zettlemoyer, *J. Am. Chem. Soc.*, **66**, 1402, 1405 (1944) ($NH_4H_2PO_4$). C. C. Stephenson and H. E. Adams, *ibid.*, 1409 (1944) ($NH_4H_2AsO_4$).

for $NH_4H_2PO_4$, $ND_4D_2PO_4$, KH_2PO_4, KD_2PO_4, RbH_2PO_4, as well as for the arsenates of NH_4, K, Rb, and Cs, both as the dihydrogen and dideuterium salts. No such transition is found for CsH_2PO_4 and RbD_2PO_4, perhaps because of the formation of a metastable form. The "lower Curie points" do not show any order-disorder transitions, and it is thought that they correspond to a freezing in of the dipoles' mobility. An example of the λ-type specific heat anomaly is shown in Figure 9-14. For comparison's sake, it should be noted that Rochelle salt does not exhibit a specific-heat anomaly at its Curie point.

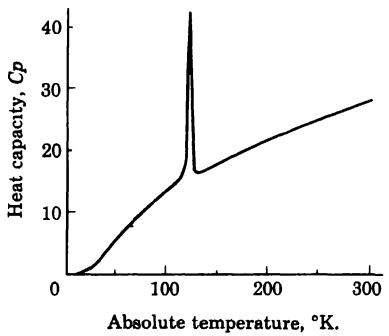


Fig. 9-14. Heat capacity curve for monopotassium orthophosphate, KH_2PO_4, showing the anomaly at the Curie point.

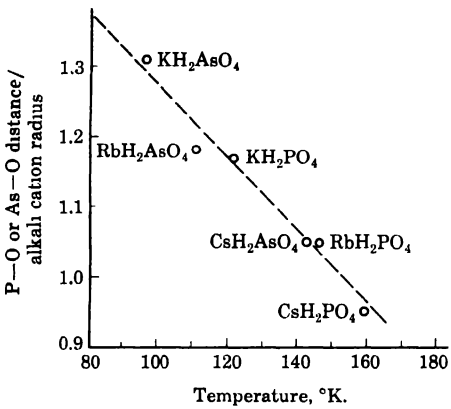


Fig. 9-15. The ferroelectric transition temperatures for monoalkali phosphates and arsenates.

The dielectric transition (Curie point) and the order-disorder transition, found at the same temperature by specific heat measurements, correspond to a crystallographic transition as well. X-ray structure studies on monopotassium phosphate show a transition from the higher temperature tetragonal to an orthorhombic (ferroelectric) structure at the Curie point.[60]

The transition temperatures for the various dihydrogen orthophosphates and arsenates appear to be approximately proportional to the cation/anion size-ratio, as shown in Figure 9-15. It should also be noted that the dielectric constant of the salts becomes smaller the larger the cation is with respect to the XO_4 anion.

[60] B. C Frazer and R. Pepinsky, *Acta Cryst.*, **6**, 273 (1953); *Phys. Rev.*, **85**, 479 (1952); R. Pepinsky, *Abstracts of meeting, American Crystallographic Association, Harvard University, April 5–9, 1954, paper No. 24.*

In 1941 a statistical theory for ferroelectricity in the monoalkali orthophosphates was developed by Slater.[61] According to this idea, an ordering of the hydrogen atoms takes place in such a way that in one domain the hydrogens are more closely associated with the upper oxygens of all of the PO_4 groups and in another domain with the lower oxygens in the structure. Dipoles based on $H_2PO_4^+$, with orientation parallel or antiparallel to the *c*-axis, are then presumed to account for the spontaneous polarization.

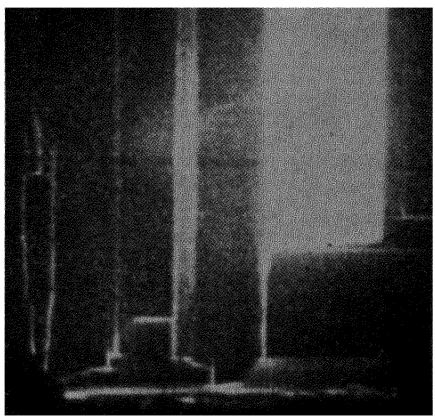


Fig. 9-16. Photomicrograph of the domains in monopotassium orthophosphate in its ferroelectric phase.

X-ray and neutron diffraction studies[60,62] indicate that the alignment of the hydrogens does not fully account for the effect, but that there is also a displacement of the phosphorus atom within its tetrahedron of surrounding oxygens. The x-ray data also indicate that the thermal vibrations in the ferroelectric crystal are anisotropic, with maximum displacement along the *c*-axis.

[61] J. C. Slater, *J. Chem. Phys.*, **9**, 16 (1941). Also see the following papers for modifications: A. van Aix, *Helv. Phys. Acta*, **22**, 403 (1949); T. Nagamiya and S. Yomosa, *J. Chem. Phys.*, **17**, 102 (1949); J. Pirenne, *Helv. Phys. Acta*, **22**, 479 (1949); *Physica*, **15**, 1019 (1949); G. Shirane and T. Oguchi, *J. Phys. Soc. Japan*, **4**, 172 (1949); Y. Takagi, *Proc. Phys.-Math. Soc. Japan*, **23**, 1069 (1941); *Proc. Phys. Soc. Japan*, **3**, 80 (1948); and *J. Phys. Soc. Japan*, **3**, 273 (1948) (the latter is in English).

[62] S. W. Peterson, H. A. Levy, and S. H. Simonsen, *J. Chem. Phys.*, **21**, 2084 (1953); H. A. Levy, S. W. Peterson, and S. H. Simonsen, *Phys. Rev.*, **93**, 1120 (1954); G. E. Bacon and R. S. Pease, *Proc. Roy. Soc.*, **220A**, 397 (1953); *ibid.*, **230A**, 359 (1955).

The domain structure in monopotassium orthophosphate has been observed directly.[63] A photomicrograph of the domains as observed by Mitsui and Furuichi is given in Figure 9-16.

Ammonium dihydrogen orthophosphate and arsenate are not ferroelectrics, but they exhibit properties which are related to those of the ferroelectric phosphates. They crystallize with the same tetragonal symmetry as the ferroelectric salts exhibit above their Curie points. Their dielectric constants increase as they are cooled down from room temperature, and there are low-temperature transitions with specific heat anomalies very

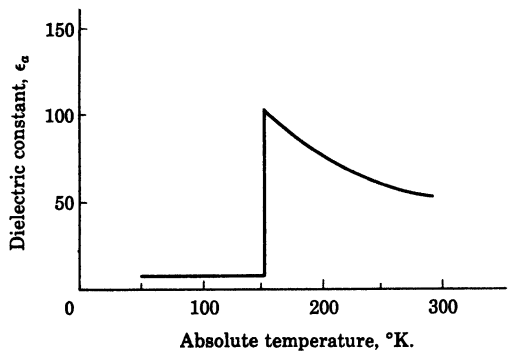


Fig. 9-17. Variation of the dielectric constant of monoammonium phosphate with temperature.

similar to those of the potassium salts. However, there is no ferroelectric transition. The temperature variation of the dielectric constant (ϵ_a) measured along the *a*-axis of ammonium dihydrogen phosphate is shown in Figure 9-17. The dielectric constant measured along the *c*-axis behaves in much the same way, except that its maximum value is only approximately a quarter of the maximum value for ϵ_a.

Mixed crystals have been studied to throw more light on the nature of the transitions found in the ammonium dihydrogen phosphate and arsenate. Thus, investigation of the mixed ammonium-potassium salt[64] showed that addition of potassium at first depresses the transition temperature without altering the nature of the transition, but that higher percentages usher in a ferroelectric phase with Curie points lower than pure KH_2PO_4. A similar study has been carried out on the mixed ammonium-rubidium

[63] T. Mitsui and J. Furuichi, *Phys. Rev.*, **90**, 193 (1953); M. deQuervain and B. Zwicker, *Helv. Phys. Acta*, **16**, 216 (1943).

[64] I. Nitta, R. Kiriyama, and M. Haisa, *Sci. Papers Osaka Univ.*, **30**, 1 (1951).

dihydrogen phosphate[65] to give the same kind of results. These studies and others have led to the conclusion that ammonium dihydrogen phosphate is an antiferroelectric material.[66] This means that domains are formed, but the domains in which the dipoles are directed parallel to the *c*-axis are counterbalanced by domains in which the dipoles are oppositely directed (antiparallel to the *c*-axis).

Because of their possible use in constructing very small condensers of high capacity, the ferroelectrics have been the subject of considerable study during recent years. Much of this work has been supported by the Armed Services, who are interested in developing miniature electronic circuits for use in guided missiles.

Piezoelectricity and Other Electrical Phenomena

The same orthophosphates which exhibit ferroelectric behavior have found considerable application as piezoelectric crystals. A piezoelectric crystal[67] may be defined as one in which electricity or electric polarity is produced by pressure; or, more briefly, as one which becomes electrified when deformed or conversely becomes deformed when placed in an electric field. This property of piezoelectricity is a very general one found in all noncentrosymmetric crystals. Of the 32 crystal classes, 20 exhibit piezoelectricity.

The dihydrogen orthophosphates of potassium, rubidium, cesium, thallium, and ammonium have all been considered in piezoelectric applications. Of these, probably the most information is available on the ammonium and potassium salts, $NH_3H_2PO_4$ and KH_2PO_4. The potassium salt lies in the ditetragonal-alternating crystal class (hemihedral with inversion axis, Shoenfliess symmetry: V_d) for which there are two different piezoelectric constants, d_{36} and d_{14}. At the Curie point, d_{36} has a value[68] as high as $60{,}000 \times 10^{-8}$, but at room temperature the value levels off around 50×10^{-8} Below the Curie point, there is also a diminution in d_{36} which decreases to $10{,}000 \times 10^{-8}$ at the temperature of liquid air. Below the Curie point, the piezoelectric constant is a function of stress as well as temperature, so that hysteresis curves can be obtained, and the polarization is no longer proportional to the stress.

[65] R. Keeling, Thesis, Pennsylvania State College, State College, Penn., 1952.

[66] W. P. Mason, *Phys. Rev.*, **88**, 480 (1952); T. Nagamiya, *Sci. Papers Osaka Univ.*, **29**, 1 (1951).

[67] For general information see such a book as W. G. Cady, *Piezoelectricity*, McGraw-Hill Book Co , New York, 1946.

[68] W. Ludy, *Z. Phys* , **113**, 302 (1939); *Helv. Phys. Acta*, **12**, 278 (1939); W. Bantle and B. Matthias, *Helv. Phys. Acta*, **18**, 242 (1945); W. Bantle and C. Calfisch, *ibid.*, **16**, 235 (1943).

At ordinary temperatures, both monopotassium and monoammonium orthophosphates are so far above their Curie points as to give straightforward piezoelectric effects, in which the e.m.f. is proportional to the distorting force, with essentially no hysteresis. In both its mechanical and piezoelectric properties, KH_2PO_4, like the other phosphates, stands between quartz and Rochelle's salt. As compared to quartz, its piezoelectric effect is about seven times as great; however, some of its elastic temperature coefficients are also somewhat greater than those of quartz. As compared to Rochelle's salt, it is more stable to moisture, having no water of crystallization and does not show the complicated behavior exhibited by Rochelle's salt in the neighborhood of its Curie point at 24°C. Because of these properties, the orthophosphates have received very favorable consideration for applications based on piezoelectricity.[69] Considerable literature[70] has been devoted to the art of growing suitable crystals of KH_2PO_4 and $NH_2H_2PO_4$ for piezoelectric applications.

This same group of orthophosphates can act as a solid electro-optic shutter;[71] since, when a voltage is applied in the Z direction to a basal section of the crystal, it becomes biaxial. When a beam of light is to be turned on and off rapidly by means of an electric current, these orthophosphate crystals are to be preferred to the usual Kerr cell, since they are solids and can readily be built into equipment so that continued upkeep of the system is not necessary.

CALCIUM ORTHOPHOSPHATES

Calcium Orthophosphates from Aqueous Solution

Five calcium phosphates which exhibit distinct and different x-ray diffraction patterns can be obtained by precipitation from aqueous solution at normal pressures. These are (1) anhydrous monocalcium phosphate, $Ca(H_2PO_4)_2$, (2) monocalcium phosphate monohydrate,[72] $Ca(H_2PO_4)_2 \cdot H_2O$,

[69] For a survey of crystals exhibiting piezoelectricity, see P. H. Egli, *Am. Mineralogist*, **33**, 622 (1948).

[70] For example, A. E. Robinson, *Discussions Faraday Soc.*, **1949**, No. 5, 315; L. Kramer, *Chem. Inds.*, **63**, No. 1, 40 (1948); A. C. Walker, *Bell Labs. Record*, **25**, 357 (1947); H. J. Kolb and J. J. Comer, *J. Am. Chem. Soc.*, **67**, 844 (1945). Also see the following patents: U S Pat. 2,615,797; U. S. Pat. 2,575,511; U. S. Pat. 2,546,305; U. S. Pat. 2,484,829; Brit. Pat. 666,877; Fr. Pat 935,743; and Swiss Pat. 276,135.

[71] B. H. Billings, *J. Opt. Soc. Amer.*, **39**, 797 (1949); R. O'B. Carpenter, *ibid.*, **40**, 225 (1950); also see B. Zwicker and P. Sherrer, *Helv. Phys. Acta*, **17**, 346 (1944); P. Mokry, *Czechoslov. J. Phys.*, **2**, 145 (1953).

[72] H. Bassett, *Proc. Chem Soc.*, **22**, 315 (1907).

(3) anhydrous dicalcium phosphate, $CaHPO_4$, (4) dicalcium phosphate dihydrate,[72] $CaHPO_4 \cdot 2\,H_2O$, and (5) a crystalline precipitate of variable composition having the x-ray pattern of an apatite.[73] This latter precipitate is an hydroxylapatite, for which the base formula, $Ca_5(OH)(PO_4)_3$, is usually written, although this formula does not take into account the variable composition or the amount of hydration. A number of other crystalline calcium orthophosphates (in the system CaO–H_2O–P_2O_5) are alleged to have been prepared from solution, but none of these materials has been proven to exist. Many of them, such as "tricalcium phosphate," are designations given to various hydroxylapatite compositions which have arbitrarily been singled out from the hydroxylapatite family.

The literature on the calcium phosphates is very voluminous--running to thousands of papers, if technological as well as scientific writings are included. A considerable proportion of this literature deals with phosphates which exhibit the x-ray diffraction pattern of hydroxylapatite.* The so-called precipitated "tricalcium phosphate" is an hydroxylapatite for which the Ca/P mole ratio ranges about the value of $^3/_2$. Indeed, the "tricalcium phosphate" of commerce is an hydroxylapatite of this type. Hydroxylapatite for which Ca/P lies near $^4/_3$ has also been called "octacalcium phosphate" or "octaphosphate" for short. Not only is the terminology of the precipitated hydroxylapatites somewhat confused, but different preparations called by a given name may be far from identical. Thus, free lime, $Ca(OH)_2$, and dicalcium phosphates may be present to considerable proportions in some preparations of "tricalcium phosphate"; and, of course, substances showing nearly identical apatite x-ray powder may have considerably different Ca/P mole ratios, ranging between the approximate limits of 1.33 and 2.0.[73]

Monocalcium phosphate as either the anhydrous salt or the monohydrate can be prepared as well-formed, pure crystals by lowering the temperature of an aqueous, acidic solution. Quantitative information pertinent to this preparation is presented in Figure 9-18. Similarly, anhydrous dicalcium phosphate can also be crystallized from acidic solution; but, because of its retrograde solubility, the temperature must be raised to form a precipitate. Again, Figure 9-18 gives the needed solubility data. The dihydrate of dicalcium phosphate is more difficult to make in a pure form. A

* In this text any compound in the CaO-H_2O–P_2O_5 system which exhibits an x-ray diffraction pattern which is very similar to the accepted pattern for hydroxylapatite will be called an hydroxylapatite. This term is used herein to cover a range of compositions

[73] W. F. Neuman and M. W. Neuman, *Chem. Revs.*, **53**, 1 (1953.)

recent publication[74] recommends that it be made by slowly adding a lime-sugar solution (calcium sucrate) to dilute phosphoric acid at 10°C.

A large number of different preparations of precipitated hydroxylapatites have been described in the literature, and reference to these different preparations can be found in recent reviews.[73,75,76] Compositions corresponding closely to the formula $Ca_5(OH)(PO_4)_3 \cdot x\ H_2O$ can be prepared in a finely divided form by boiling monocalcium phosphate dihydrate with calcium carbonate[77] or by slowly reacting an alkaline phosphate with a soluble calcium salt such as the nitrate.[78] Larger crystals, approximately 0.2 mm.

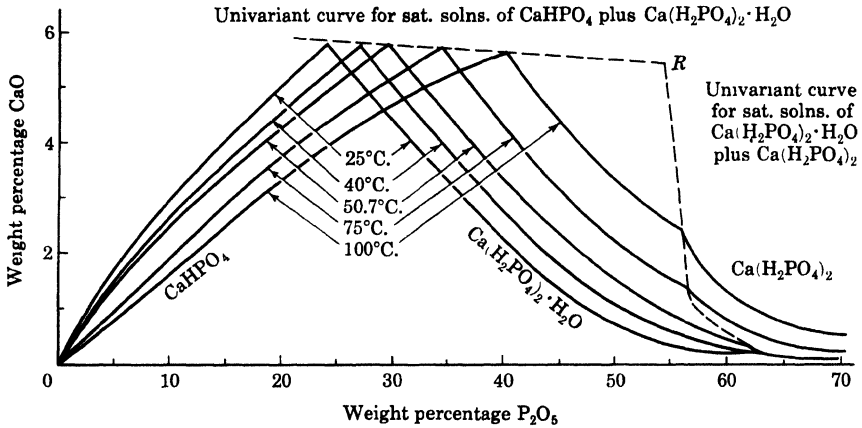


Fig. 9-18. The system $CaO–H_2O–P_2O_5$ for the calcium orthophosphates at 25, 40 50.7, 75, and 100°C. *R* is the quintuple point between $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca(H_2PO_4)_2$, $CaHPO_4$, saturated solution, and saturated vapor.

long, having an over-all composition very close to the above formula have been made in the form of prisms by hydrothermal synthesis.[79] The "tri-

[74] P. D. S. St. Pierre, *J. Am. Chem. Soc.*, **77**, 2197 (1955). For another related preparation see J. Melon and M. J. Dallemagne, *Bull. soc. chim. Belges*, **55**, 38 (1946).

[75] D. Carlström, *Acta Radiologica, Supp. 121*, 1-59 (1955); E. B. Jaffe, *Geological Survey Circular No. 135, Abstracts of the Literature on Synthesis of Apatites and Some Related Phosphates*, U. S. Geol. Survey, Washington, D. C., 1951, 77 pp.

[76] S. Eisenberger, A. Lehrman, and W. D. Turner, *Chem. Revs.*, **26**, 257 (1940).

[77] W. Rathje, *Bodenkunde u. Pflanzenernahr.*, **12**, 121 (1939).

[78] E. Hayek and W. Stadlmann, *Angew. Chem.*, **67**, 327 (1955); G. Tromel and H. Möller, *Z. anorg. u. allgem. Chem.*, **206**, 227 (1932); and others.

[79] A. Perloff and A. S. Posner, *Science*, **124**, 583 (1956); also see E. Hayek, J. Lechleitner, and W. Bohler, *Angew. Chem.*, **67**, 326 (1955); private communications from E. Hayek and A. Posner.

calcium phosphate" of commerce is usually prepared by adding phosphoric acid to a lime slurry, filtering, and drying. The neutralization of phosphoric acid with lime has been the subject of considerable study.[80] This work has shown that the usual titration curve of phosphoric acid is obtained up to a region somewhere beyond the first neutralization point near pH 4. Then, monocalcium phosphate precipitates. After a little more than one equivalent of calcium hydroxide has been added, further gradual addition of lime tends to *lower* the pH until a Ca/P mole ratio of about 3 has been exceeded. X-ray and other studies of precipitates corresponding to Ca/P mole ratios greater than unity show that mixtures of the usual crystalline calcium phosphates plus occasional amorphous material are commonly present. At room temperature, and even at boiling temperatures, equilibrium is very slowly, if ever in some cases, obtained with respect to the precipitated solids.

Aqueous Phase Diagrams of Calcium Orthophosphates

The phase diagram[81] for the calcium orthophosphates at 25°C. is given in Figure 9-19, in which the various solid alkaline calcium phosphates of the type exhibiting the hydroxylapatite x-ray diffraction pattern are indicated by a large indeterminate area of composition in the small-scale plot (part *B*). In part *A* of this figure, the region near the origin is approximated on a greatly expanded scale, from which it can be seen that dicalcium phosphate dihydrate has a very limited region of solubility at 25°C., and that the hydroxyapatite compositions are extremely insoluble. The only region of reasonably high solubility in the entire system is in the acid range,[82] with the highest solubility of 24.1 wt.-% P_2O_5 and 5.79 wt.-% CaO

[80] G. H. Wendt and A. H. Clarke, *J. Am. Chem. Soc.*, **45**, 881 (1923); G. Fouretier, *Compt. rend.*, **205**, 413 (1937); L. E. Holt, V. K. La Mer, and H. B. Chown, *J. Biol. Chem.*, **64**, 509 (1925); R. G. W. Farnell, *J. Soc. Chem. Ind., Trans.*, **45**, 343 (1926); I. Greenwald, *J. Am. Chem. Soc.*, **66**, 1305 (1944); M. J. Dallemagne and J. Melon, *Bull. soc. chim. biol.*, **28**, 566 (1946); *Bull. soc. chim. Belges*, **56**, 180 (1947). Also many other papers.

[81] K. L. Elmore and T. D. Farr, *Ind. Eng. Chem.*, **32**, 580 (1940); H. Bassett, *Z. anorg. Chem.*, **53**, 34, 49 (1907); *ibid.*, **59**, 1 (1908); *J. Soc. Chem. Ind. (London)*, **28**, 722 (1910); *J. Chem. Soc.*, **111**, 620 (1917); J. d'Ans and R. Knutter, *Angew. Chem.*, **65**, 578 (1953); also see F. K. Cameron, *J. Am. Chem. Soc.*, **32**, 869 (1910); F. K. Cameron and A. Seidell, *ibid.*, **27**, 1503 (1905); A. P. Belopol'skii, A. A. Taperova, M. T. Serebrennikova, and M. N. Shul'gina, *J. Chem. Ind. U.S.S.R.*, **14**, 504 (1937); A. V. Kazakov, *Trans. Sci. Inst. Fertilizers Insectofungicides*, **139**, 3 (1937).

[82] The density, electrical conductivity, and pH of various solutions of calcium phosphates have been reported by A. J. Smith and E. O. Huffman, *Ind. Eng. Chem., Chem. & Eng. Data Series*, **1**, 99 (1956).

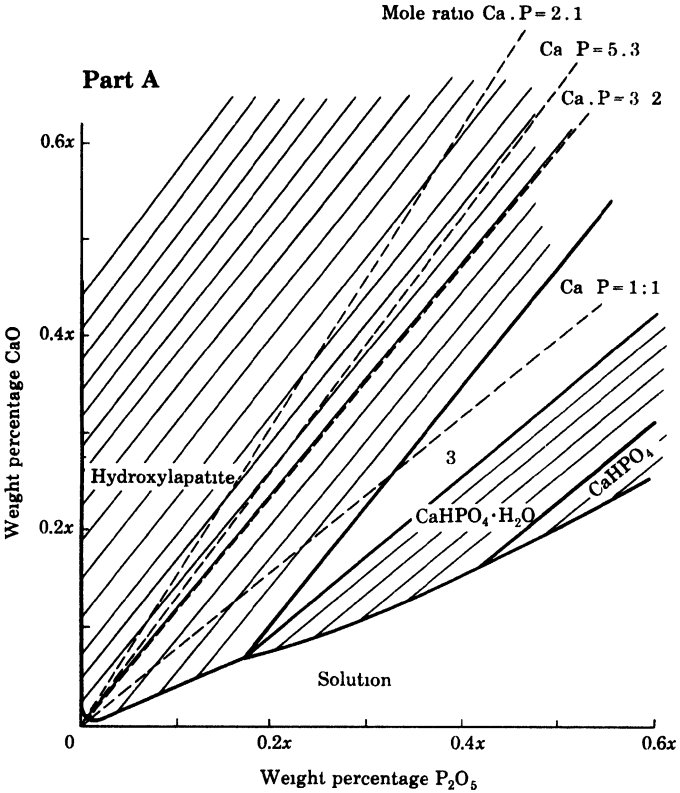
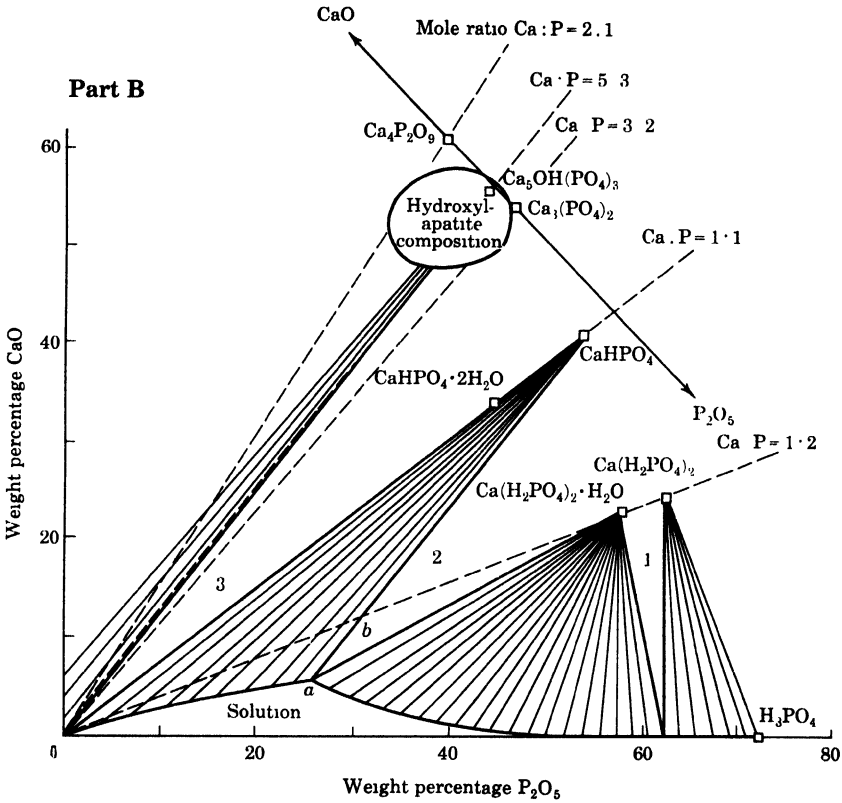


Fig. 9-19 The system CaO–H_2O–P_2O_5 for the calcium orthophosphates at 25°C. Part A (above) represents a one hundred- to four hundred-fold magnification of the origin of part B (facing page) of this figure. Part B is based on precise data, but part A is only an approximation. According to the data of Bassett, x in part A is 1; according to d'Ans and Knutter, x is about $^1/_3$–$^1/_4$.

at 25°C. corresponding to the invariant point at which $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4$ are in equilibrium with this solution. The three-phase areas in Figure 9-19 are numbered. They are (1) anhydrous $Ca(H_2PO_4)_2$ plus $Ca(H_2PO_4)_2 \cdot H_2O$ plus solution, (2) $Ca(H_2PO_4)_2 \cdot H_2O$ plus anhydrous $CaHPO_4$ plus solution, and (3) $CaHPO_4 \cdot 2\ H_2O$ plus hydroxylapatite plus solution.

In Figure 9-18 the most soluble region of the calcium orthophosphate phase diagram is plotted as a function of temperature. From this plot it should be noted that the solubilities of both $Ca(H_2PO_4)_2$ and $Ca(H_2PO_4)_2 \cdot H_2O$



in acid solution increase with rising temperature, whereas the solubility of $CaHPO_4$ in acid solution decreases with rising temperature. The phosphorus content of the saturated solution in equilibrium with both crystalline phases, $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4$, is seen to increase considerably with temperature, whereas the calcium content of this same saturated solution diminishes only slightly with increasing temperature. On the other hand, the relative change with temperature of the calcium content of the saturated solution in equilibrium with both $Ca(H_2PO_4)_2$ and $Ca(H_2PO_4)_2 \cdot H_2O$ is much greater than that of the phosphorus. Extrapolation of these two invariant curves showing the change in concentration of the two saturated solutions with temperature leads to a quintuple point (*R* in Fig. 9-18) at which the three solids $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca(H_2PO_4)_2$, and $CaHPO_4$ are in equilibrium with a saturated solution containing 5.2 wt.-% CaO and 54.5

wt.-% P_2O_5 and with a certain water vapor pressure. The extrapolated temperature of this quintuple point is about 160°C.

The data of Elmore and Farr[81] extrapolated to a temperature of 165°C. and those of H. Bassett extrapolated to 153°C. for the temperature of this quintuple point (see ref. 81). Bassett[81] finds 5.6 wt-% CaO and 54.0 wt-% P_2O_5 at this point.

At temperatures about 160°C. monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$, no longer appears on the phase diagram. According to Bassett[81] there are two other quintuple points in the phase diagram. One of them corresponds to equilibrium between $CaHPO_4$, $CaHPO_4 \cdot 2\ H_2O$, and hydroxyapatite plus a saturated solution believed to contain 0.05 wt.-% CaO and 0.14 wt.-% P_2O_5 and the saturated vapor. Bassett states that this quintuple point appears around 36°C. At higher temperatures the dihydrate of dicalcium phosphate, $CaHPO_4 \cdot 2\ H_2O$, should no longer appear in the phase diagram. The third quintuple point corresponds to equilibrium between $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4$, and $CaHPO_4 \cdot 2\ H_2O$ plus a saturated solution. Bassett reports some evidence to show that this quintuple point is near 20°C. However, the data of Figure 9-18 seem to indicate a much lower temperature which could even be below the ice point. Below this quintuple point, anhydrous $CaHPO_4$ should no longer occur in the phase diagram.

Because of their applicability to fertilizer technology, a number of aqueous phase-diagram studies have been made on the calcium salts of phosphoric acid with other mineral acids. Thus, the system CaO-H_2O–P_2O_5–SO_3 has been investigated by several authors.[83] The system CaO–H_2O–P_2O_5–N_2O_5 has also been studied because of nitrophosphate fertilizers.[84] In addition, there is a paper on the system CaO-H_2O–P_2O_5–HCl in which a crystalline double salt, $Ca(H_2PO_4)_2 \cdot CaCl_2 \cdot 2\ H_2O$ or $Ca_2H_4Cl_2(PO_4)_2 \cdot 2\ H_2O$ is found.[85] A related study on the system CaO–H_2O–P_2O_5–HF delineated the solubility region of fluorapatite.[86] A very thorough investigation

[83] A. N. Campbell and J. W. Coutts, *Ind. Eng. Chem.*, **40**, 1295 (1948); A P. Belopol'skii, A. A. Taperova, M. T. Serebrennikova, and M. N. Shul'gina, *J. Chem. Ind. U.S.S.R.*, **14**, 660 (1937); also see E. Thilo, *Z. Phys. Chem.*, **A148**, 361 (1930) for a study of the dissolution of calcium phosphates in sulfurous acid.

[84] A. P. Belopol'skii, M. N. Shul'gina, M. T. Serebrennikova, and S. Ya. Shpunt, *J. Applied Chem. U.S.S.R.*, **10**, 403 (1937); *ibid.*, **10**, 1523 (1937); I Tananoev, S. Chrelashvili, and N. Sheliya, *Trudy Tbilis. Khim. Inst. Grucinskii Filial Akad. Nauk*, **8**, 159 (1940).

[85] A. A. Taperova and M N. Shul'gin, *J. Applied Chem. U.S.S.R.*, **19**, 1350 (1946)

[86] A. V. Kazakov, *Akad. Nauk. U.R S.S., Geol. ser.*, **144**, No. 40, 1 (1950).

has been carried out on the more complex system Ca^{2+}-NH_4^+–H^+-PO_4^{3-}–NO_3^-–H_2O by Flatt and coworkers.[87]

Although the phase diagram studies described in the preceding paragraph indicate that calcium chloride and calcium nitrate solutions have a strong salting-out effect on the phosphates, it is generally found that dicalcium phosphate and hydroxylapatite compositions exhibit abnormally high solubilities[87a] in solutions of a large number of weak acids, as well as in solutions of most highly soluble salts containing cations other than calcium. Thus, carbon dioxide exerts a strong dissolving action on both the anhydrous and dihydrate forms of monocalcium phosphate,[88] as well as on the "tricalcium phosphate" composition of hydroxylapatite. A recent study[89] of the ability of a large number of organic acids to dissolve dicalcium phosphate and hydroxyapatite clearly indicated that the reaction is not solely dependent on the pH of the solution used, but that it is also dependent on structural characteristics of the acid. Related to this is the standard technique[90] of measuring availability of fertilizers, which depends on the solubility of the calcium phosphates in ammonium citrate. In addition to ammonium citrate, solutions of such simple salts[87a] as sodium chloride, potassium sulfate, ammonium nitrate, etc. have a better dissolving action on dicalcium phosphate and hydroxyapatite than does pure water.

Properties and Reactions of Calcium Orthophosphates

Both monocalcium phosphate and dicalcium phosphate dissolve incongruently in water—that is to say, their dissolution in water is accompanied by reaction. This reaction can best be explained by referring to the phase diagram of aqueous calcium orthophosphates.

[87] R. Flatt, *Helv. Chim. Acta*, **33**, 2029 (1950); R. Flatt and P. Fritz, *ibid.*, **33**, 2045 (1950); *ibid.*, **34**, 231 (1951); R. Flatt, G. Brunisholz, and S. Chapuis-Gottreux, *ibid.*, **34**, 683, 884 (1951); R. Flatt, G. Brunisholz, and P. Clerc, *ibid.*, **34**, 2348 (1951); *ibid.*, **35**, 336 (1952); R. Flatt, G. Brunisholz, and E. Lauber, *ibid.*, **36**, 1971, 1980 (1953); R. Flatt, G. Brunisholz, and M. Jaunin, *ibid.*, **37**, 282 (1954); R. Flatt, *ibid.*, **37**, 299 (1954); R. Flatt, J. Wilhelm, G. Brunisholz, and G. Fell, *ibid.*, **37**, 607 (1954).

[87a] J. W. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1923, Vol. 3, pp. 864–907.

[88] A. Rindell, *Untersuchungen uber Loslichkeit einiger Kalkphosphate*, Thesis, Univ. of Helsingfors, 1899.

[89] H. W. Johnston, *New Zealand J. Sci. Technol.*, **33B**, 436 (1952).

[90] Assoc. Official Agric. Chemists, *Official Methods of Analysis*, 7th ed., Washington, D. C., 1950, pp. 10–11. Also see K. D. Jacob and W. L. Hill, *Soil and Fertilizer Phosphorus*, ed. W. H. Pierre and A. G. Norman, Academic Press, New York, 1953, pp. 299–346.

In Figure 9-19, it should be noted that, if water is gradually added to anhydrous monocalcium phosphate, $Ca(H_2PO_4)_2$, equilibrium conditions will first correspond to a mixture of the anhydrous salt and its monohydrate. After complete conversion to the monohydrate has occurred, there will be reaction with water to form at equilibrium anhydrous dicalcium phosphate according to the following equation.

$$Ca(H_2PO_4)_2 \cdot H_2O + x\ H_2O = CaHPO_4 + H_3PO_4 + (x + 1)\ H_2O \qquad (9\text{-}15)$$

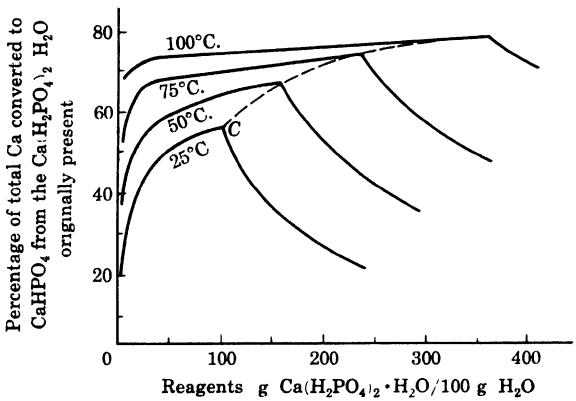


Fig. 9-20 Conversion of monocalcium phosphate monohydrate into anhydrous dicalcium phosphate by the action of water, according to equation 9-15 The lines to the right of the dotted line correspond to mixtures of two solids ($CaHPO_4$ and some original $Ca(H_2PO_4)_2 \cdot H_2O$), whereas the lines to the left correspond to only one solid ($CaHPO_4$). Point C in this figure is equivalent to point b in Figure 9, Part B.

By adding water, so as to follow down the line corresponding to Ca/P = $^1/_2$ in Figure 9-19, it is seen that one enters a region (region 2) where $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4$ are in equilibrium with the saturated solution marked *a*. As water is added, the proportion of crystalline $CaHPO_4$ to crystalline $Ca(H_2PO_4)_2 \cdot H_2O$ increases until just beyond point *b* there is no $Ca(H_2PO_4)_2 \cdot H_2O$ left. Continuing down the line corresponding to Ca/P = $^1/_2$, the amount of solid (now only $CaHPO_4$) decreases so that the solution becomes more alkaline. The conversion of monocalcium phosphate by the hydrolysis process of equation 9-15 is depicted in Figure 9-20 for several different temperatures. Point *C* in Figure 9-20 corresponds to point *b* in Figure 9-19.

It is apparent from part A of Fig. 9-19 that dicalcium phosphate dissolves incongruently in water in the same manner as does monocalcium phosphate

(see preceding paragraph for detailed discussion). However, when dicalcium phosphate reacts with water, it forms free phosphoric acid plus an hydroxylapatite composition.

Because of the difficulty in writing a simple formula for the hydroxyapatite compositions, an equation equivalent to 9-15 will not be given for this reaction. Also, since the extreme end on the alkaline side (part A of Fig. 9-19) of the calcium orthophosphate-water phase diagram has not been determined with reasonable accuracy because of the great insolubility of the crystalline salts and the experimental difficulties of reaching equilibrium, a reasonably precise conversion diagram, similar to Figure 9-18 cannot be given.

In general, it has been found that extended treatment of any calcium phosphate with excess water leads to an apatite—hydroxylapatite if the system consists of only CaO, P_2O_5, and water. Since monocalcium phosphate and dicalcium phosphate are more acid than the apatites, they form hydroxylapatite plus phosphoric acid. Also, it is occasionally stated[91] in the literature that, when hydroxylapatite compositions for which Ca/P is either greater or less than $^5/_3$ are treated for extended lengths of time with water, the composition changes to that of the formula usually given for hydroxylapatite $Ca_5(OH)(PO_4)_3$, with more or less firmly bound water.

A number of experimental studies have been reported concerning the action of water on monocalcium phosphate[92] and on dicalcium phosphate.[93] It is obvious from published studies that the kinetics of the hydrolysis process must be very complex.

The solubility products for monocalcium phosphate monohydrate and for anhydrous dicalcium phosphate have been thermodynamically calculated in a precise manner[94] from the solubility data of Elmore and Farr at 25°C. These solubility constants are based on the assumptions that (1) the activity coefficient of calcium in the phosphate solutions is the same as its activity in calcium chloride solutions at the same ionic strength and (2) the ionic strength equals 3[Ca] + antilog (−pH). Orthophosphato-calcium complexes[97] in solution were neglected (probably a minor error) in calculating the solubility constants, which are presented on the next page:

[91] E Hayek, F. Mullner, and K. Koller, *Monatsh. Chem.*, **82,** 959 (1951); A. Schleede, W. Schmidt, and H. Kindt, *Z. Elektrochem.*, **38,** 633 (1932). Also others.

[92] For example, A. Sanfourché and B. Focet, *Compt. rend.*, **184,** 1654 (1927); *Bull. soc. chim. France,* **53,** 974 (1933).

[93] K. Buch, *Z. anorg. Chem.*, **52,** 325 (1907), A. Sanfourché and J. Henry, *Compt rend.*, **194,** 1940 (1932).

[94] T. D. Farr, "Phosphorus," *Chem. Eng. Rept. No. 8,* Tennessee Valley Authority, Wilson Dam, Alabama, 1950.

For $Ca(H_2PO_4)_2 \cdot 2\,H_2O$

$$K_{25°} = a_{Ca^{2+}} \cdot a^2_{H_2PO_4^{2-}} = 7.19 \times 10^{-2} \qquad (9\text{-}16)$$

For $CaHPO_4$ and $CaHPO_4 \cdot 2\,H_2O$

$$K_{25°} = a_{Ca^{2+}} \cdot a_{HPO_4^{2}} = 2.18 \times 10^{-7} \qquad (9\text{-}17)$$

The solubility constant calculated for anhydrous dicalcium phosphate, $CaHPO_4$, also applies to its dihydrate, the solubility of which differs from that of the anhydrous salt by the square of the activity of water at the invariant point where $CaHPO_4$ and $CaHPO_4 \cdot 2\,H_2O$ are in equilibrium. As shown in Figure 9-19 (A), this point is very close to the origin (100% H_2O), so that the activity of water there is probably greater than 0.98 or 0.99.

The solubility of compositions exhibiting the hydroxylapatite x-ray diffraction pattern has been the subject of a large amount of study because this information is thought to be needed in order to properly understand the physiology of bone growth and the equilibrium of bones with body fluids. It is also of considerable interest to the field of fertilizer technology and to the general problems of the interaction of calcium and phosphorus in the soil. A large number of "solubility constants" have been reported, but there is no consistency between the reported values[95] which vary over a range of 10^{11}. It is quite obvious from the data that the hydroxylapatite used in many of the solubility studies was contaminated by dicalcium phosphate. In a recent paper,[96] the solubility of hydroxylapatite was measured in carbonate-free water in such a manner as to show that hydroxylapatite probably exhibits a real solubility constant. The value of this constant, which was measured (1) on high-surface-area material directly after precipitation and (2) upon dissolution of the solid hydroxylapatite, is said to be given by the following equation:

$$K_{25°} = [Ca^{2+}]^{10}[PO_4^{3-}]^6[OH^-]^2 = 10^{-115} \qquad (9\text{-}18)$$

There has been some discussion[97] in the literature of soluble complexes between the calcium ion and the orthophosphate ions. From data obtained with an ion exchange resin, the dissociation constant of the soluble complex, which was formulated as $[Ca^{2+}][HPO_4^{2-}]$, was estimated to be 1.3×10^{-2}.

[95] See the review by H. C. Hodge, *Conf. on Metabolic Interrelations, Trans.*, **3**, 190 (1951).

[96] J. S. Clark, *Can. J. Chem.*, **33**, 1696 (1955)

[97] R. E. Gosselin and E. R. Coghlan, *Arch. Biochem. Biophys.*, **25**, 301 (1953). *J. Pharmacol. Exptl. Therap.*, **104**, 180 (1952), I. Greenwald, J. Redish, and A. C. Kilbrick, *J. Biol. Chem.*, **135**, 65 (1940).

Crystallographic studies[98] and x-ray structure determinations[99] have shown that there are structural similarities between the crystals of $CaHPO_4 \cdot 2\ H_2O$, $Ca(H_2PO_4)_2 \cdot H_2O$ and gypsum, $CaSO_4 \cdot 2\ H_2O$. The similarity between $CaHPO_4 \cdot 2\ H_2O$ and $CaSO_4 \cdot 2\ H_2O$ is based on the fact that the only geometrical difference between the two is the extra hydrogen of the $CaHPO_4 \cdot 2\ H_2O$. Monocalcium phosphate monohydrate has a structure similar to dicalcium phosphate dihydrate because an ($H_2PO_4^-$) group in the former substitutes for an H_2O in the latter. From a crystallographic point of view, it is thus possible to think of monocalcium phosphate monohydrate as $CaHPO_4(H_2O \cdot H_2PO_4 \cdot H)$. In the crystals of $Ca(H_2PO_4) \cdot H_2O$, $CaHPO_4 \cdot 2\ H_2O$, and $CaHPO_4$ there are four formula weights per unit cell.[99]

When monocalcium phosphate monohydrate is heated rapidly in the open air, it undergoes partial fusion in its water of crystallization at temperatures in the range of 150–200°C. The resulting mixture is converted to stable β-calcium metaphosphate at 600–700°C. Thermal analysis[100] indicates that, on slow heating, the water of hydration of $Ca(H_2PO_4)_2 \cdot H_2O$ is lost at 150–180°C.

The thermal dehydration of the dihydrate of dicalcium phosphate has been studied by a number of investigators[101] who found several different courses of dehydration as studied by thermogravimetric techniques. Unpublished studies[102] have indicated that the rate of dehydration is strongly catalyzed by the presence of water vapor and by traces of acids. Thus, a sample of dicalcium phosphate dihydrate kept in a vacuum showed no signs

[98] J. P. Smith, J. R. Lehr, and W. E. Brown, *Am. Mineralogist*, **40**, 893 (1955); W. L. Hill and S. B. Hendricks, *Ind. Eng. Chem.*, **28**, 440 (1936); W. F. Bale, J. F. Bonner, H. C. Hodge, H. Adler, A. R. Wreath, and R. N. Bell, *Ind. Eng. Chem., Anal. Ed.*, **17**, 491 (1945); J. Melon and M. J. Dallemagne, *Ann. soc. géol. Belg., Bull.*, **69**, Nos. 1, 2, 3, B19-27 (1945–46).

[99] C. A. Beevers and B. Raistrick, *Nature*, **173**, 542 (1954); G. MacLennan and C. A. Beevers, *Acta Cryst.*, **8**, 579 (1955); also private communication from B. Raistrick.

[100] W. L. Hill, S. B. Hendricks, E. J. Fox, and J. G. Cady, *Ind. Eng. Chem.*, **39**, 1667 (1947).

[101] S. I. Vol'fkovich and V. V. Urusov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **4**, 341 (1951). A. Boullé, *International Union Pure Applied Chem., Colloquium of Section for Inorganic Chemistry, Muinster*, **2–6** *Sept.*, **1954**, Verlag Chemie, Weinheim, Germany, 1954, p. 217, H. Bassett, *Z. anorg. u. allgem. Chem.*, **54**, 1 (1908); *J. Chem. Soc.*, **3**, 620 (1917); F. Cameron and A. Seidell, *J. Am. Chem. Soc.*, **27**, 1508 (1905); A. P. Velopol'skii, A. A. Taperova, M. T. Serebrennikova, and M. N. Shul'gina, *J. Applied Chem. (U.S.S.R.)*, **14**, 504 (1937); A. V. Kazakov, *Trans. Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.)*, **139**, Chem.-Tech. Ed. (1937).

[102] T. W. Schilb, private communication reporting work done at the Monsanto Chemical Co.

of decomposition when held at a temperature of 110°C. for an extended length of time. However, immediately after allowing atmospheric air into the system, decomposition took place. Vol'fkovich and Urusov[101] have found that, depending on the partial pressure of water vapor in the gas phase which is in contact with the salt, the process of dehydration proceeds by three distinct paths. According to these authors, when the water vapor pressure is in the range of 25–100 mm. Hg, dehydration takes place in three steps at 100–110°C., 127–142°C., and 172–175°C. When the water vapor pressure ranges from about 125 to 220 mm. Hg, the dehydration of $CaHPO_4 \cdot 2\ H_2O$ has the character of a single-step process in which water is vaporized from the salt at a temperature of 68–69°C. At higher partial pressures of water, the dehydration process occurs in a single step at 68–69°C. with the formation of an intermediate liquid phase.

The kinetics of the reaction of phosphoric acid on hydroxylapatite has been studied to some extent.[103] It is found that the kinetics of the decompostion of apatite obey the classical laws of physical chemistry in that the speed of decomposition at any given time is proportional to the hydrogen ion concentration and to the surface of the solid. It is also a logarithmic function of the reciprocal of the absolute temperature. At room temperature the reaction between phosphoric acid and solid, finely divided hydroxylapatite compositions is reasonably rapid.

Since fluorapatite is the most insoluble of the calcium phosphates and calcium fluoride is also extremely insoluble, both dicalcium phosphate and the hydroxylapatite compositions react with fluoride ion.[104] At a few parts per million of fluoride in solution, chemical analysis indicates that both dicalcium phosphate and the hydroxylapatites form fluorapatite, whereas at high concentrations (several per cent of fluoride ion) the analyses are interpreted to mean that essentially all of the fluoride ion is precipitated as calcium fluoride. At intermediate concentrations of fluoride ion, mixtures of calcium fluoride and fluorapatite are said to be produced. In the case of hydroxylapatite, the exact ratio of calcium fluoride to fluorapatite depends primarily on the calcium to phosphorus ratio in the solid.

[103] M. Frey and J Byé, *Bull soc chim France*, **1950**, 1064, *ibid.*, **1950**, *Mem.* **17**, 1064, M. L. Chepelevetskii, *Trans Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.)*, **137**, 10 (1937).

[104] H. G. McCann, *J. Biol. Chem.*, **201**, 247 (1953); B Curmes, *Phosphorsaüre*, **13**, 57 (1953); T. Ramakrishnan and K. Venkatromanan, *J. Indian Inst. Sci.*, **34**, 119 (1952); G. Montel and G. Chaudron, *Compt. rend.*, **234**, 839 (1952).

Colloidal Calcium Phosphates

The hydroxylapatite compositions as usually prepared by precipitation from aqueous solutions exhibit extremely small particle sizes. An electron micrograph of particles of a pharmaceutical-grade commercial "tricalcium phosphate" is shown in Figure 9-21 It appears from this and similar photomicrographs that the individual crystallites are prisms, approximately 800 A long and 200 A in diameter Electron micrographs of other preparations of precipitated hydroxylapatite compositions have sometimes shown the existence of tabular hexagonal crystals Such crystals have

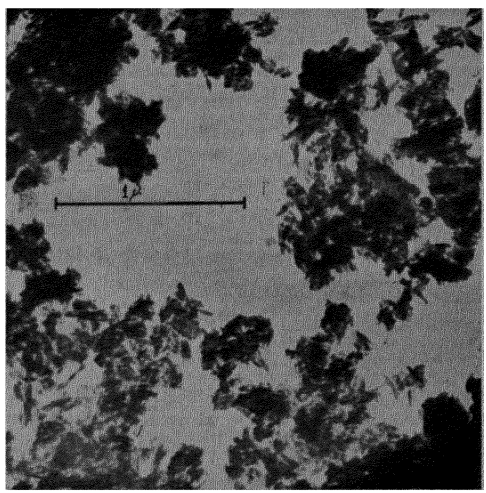


Fig 9-21 Electron microphotograph of particles of precipitated hydroxylapatite, the so-called "commercial tricalcium phosphate"

been studied in some detail as they appear in bones and bone ash Investigation[73] of the calcium phosphate crystals in bones have been carried out by (1) scattering of x-rays, (2) measurement of surface by gas adsorption and isotope exchange, and (3) direct and replication methods involving the electron microscope. It has been concluded that the average bone crystal is a hexagonal plate approximately 350 A. in length, 300 A. wide, and 25–50 A. thick, with the *c*-axis of the crystal being in the direction of the longest dimension.

The small size of the crystals of precipitated hydroxylapatite leads to interesting colloidal properties. On an average, this substance exhibits approximately 100 square meters of surface per gram. Precipitated hydrox-

ylapatite compositions,[105] as well as dicalcium phosphate,[106] have been employed as chromatographic absorbents. Some investigators using so-called "tricalcium phosphate" as a chromatographic absorbent have found large differences in the absorbing capacity of preparations from different sources. This is to be expected in view of the variable nature of precipitated hydroxylapatite.

Hydroxylapatite ("tricalcium phosphate") has found considerable industrial application as a flow conditioning agent for solids. Although this phenomenon has not received careful scientific study, it is believed that the action of finely divided hydroxylapatite in preventing powdered solids from caking and in improving flow so as to reduce their angle of repose is attributable to its (1) small particle size, (2) low electrical conductivity, and (3) ability to sorb water without becoming sticky. Simple experiments demonstrate that the particles of hydroxylapatite will pick up a considerable static charge which is not easily dispelled. Presumably, the tiny particles of hydroxylapatite act as small "roller bearings" between the particles of the poorly flowing powder, with the static charge on the hydroxylapatite acting to keep its own particles apart. For sticky, hygroscopic materials, the coating of each particle with the fine dry powder of hydroxylapatite also prevents or inhibits caking.

In a thorough colloid-chemical study of precipitated hydroxylapatite, Mattson and coworkers[107] showed that the particles behaved like those of an amphoteric colloid. At pH 11 the hydroxylapatite particles bind as much base as do the majority of clays at pH 7—with a capacity of 35–45 meq./100 g. The hydroxylapatite particles bind more sodium than potassium, and they were found to have a greater exchange capacity in sodium sulfate than in sodium chloride or in potassium chloride solutions. The particles of a given hydroxylapatite move toward either the cathode or anode depending on the pH; so that, at a certain pH, the particles do not migrate in an electric field. The pH of this isoelectric point depends on the composition of the surface layer of the crystals. In the experiments of Mattson *et al*, the isoelectric points of different preparations occurred at pH values ranging from 6.5 to 10.2.

[105] For example, S. M. Swingle and A. Tiselius, *Biochem. J.*, **48**, 171 (1951); P. M. Monaghan, H. A. Suter, and A. L. Le Rosen, *Anal. Chem.*, **22**, 811 (1950); H. J. Lennartz, *Z. anorg. u. allgem. Chem.*, **128**, 271 (1948); E. F. Hopkins, *Cornell Univ. Agri. Exp. Sta. Mem.*, **151**, 3 (1934).

[106] L. A. Moore, *Ind. Eng. Chem., Anal. Ed.*, **14**, 707 (1942)

[107] S. Mattson, E. Koutler-Andersson, R. Bruce Miller, and K. Vahtras, *Kgl. Lantsbruks Hogskol. Ann.*, **18**, 128 (1951).

The stabilization[108] of hydroxylapatite as a colloidal sol can be achieved with protective colloids such as gum arabic and gelatin. Electrolytes also serve to stabilize colloidal solutions of both hydroxylapatite and tricalcium phosphate. Liesegang rings caused by periodic precipitation of hydroxylapatite have been observed,[109] and oriented precipitation of calcium phosphate crystals has been noted[110] on the face of cleavage rhombohedra of calcite. These crystals are too small to be observed in the microscope and appear as gelatinous birefringent lamina which Gaubert called "liquid crystals" of calcium phosphate.

Melt Phase Diagrams of Calcium Phosphates

Study of the binary system CaO–P_2O_5 has been beset with many difficulties. Extremely high temperatures are reached in the orthophosphate region of composition, and the melts are quite reactive both with respect to reduction to elemental phosphorus and with respect to dissolving the container. Furthermore, interpretation of the data has often been beclouded by failure to recognize the presence of a ternary system through the inclusion of small quantities of water.[76] Thus, in the ignition of hydroxylapatite preparations in which the Ca/P mole ratio is approximately $^5/_3$ or less, it is said that elimination of water is not complete under 1500°C. Trömel[111] has also shown that hydroxylapatite can be formed from CaO–P_2O_5 binary mixtures by reaction with water vapor at temperatures as high as 1050°C.!

An imaginative interpretation of the published data[111,112] is presented in the phase diagram given in Figure 9-22. It should be noted that the temperatures in this diagram, as well as the limits of the phase boundaries are only approximate. In addition, the phase regions marked by (?) are highly questionable and are based only on a hint given in the work of Bredig, Franck, and Füldner. The first phase diagram published by these authors, although it did not represent true equilibrium conditions, is of interest in that it indicates the transformations which may be expected

[108] L. K. Lapinskii, *Vologda Dairy Inst. Bull.*, **76**, 7 (1929); G. M. De Toni, *Kolloid-Z*, **28**, 145 (1921); also see A. Mazzucchelli and D. Vita, *Gazz. chim. ital.*, **50** (I), 232 (1920).

[109] R. J. Doyle and H. Ryan, *Proc. Roy. Irish Acad.*, **38B**, 435 (1929).

[110] P. Gaubert, *Compt. rend.*, **174**, 1115 (1922).

[111] G. Tromel, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch., Dusseldorf*, **14**, 25 (1932); *Z. physik. chem.*, **158A**, 422 (1932); *Phosphorsaure*, **2**, 116 (1932); G. Tromel and H. Möller, *Z. anorg. u. allgem. Chem.*, **206**, 227 (1932); F. Korber and G. Trömel, *Z. Elektrochem.*, **38**, 578 (1932); *Archiv. Eisenhuttenw.*, **7**, 7 (1933).

[112] M. A. Bredig, H. H. Franck, and H. Fuldner, *Z. Elektrochem.*, **39**, 959 (1933). For an earlier, incorrect presentation by these same authors, see *ibid.*, **38**, 158 (1932).

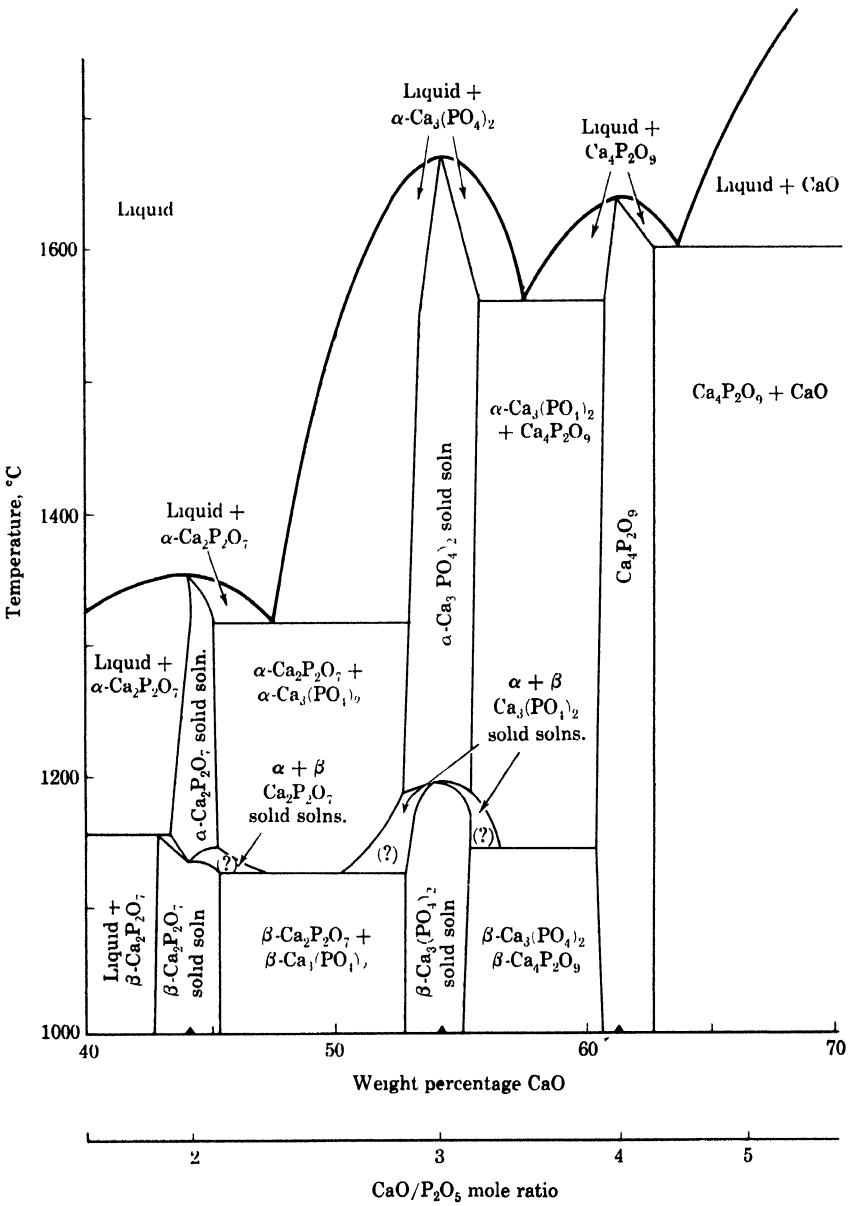


Fig. 9-22. An approximation to the CaO-P_2O_5 phase diagram between $2CaO \cdot P_2O_5$ and CaO in the absence of moisture.

when ignitions are carried out in the presence of moisture. According to this first study, the only calcium phosphate in the solid region corresponding to temperatures below about 1400°C. and to compositions containing more than about 55% CaO is hydroxylapatite (arbitrarily named α-$Ca_3(PO_4)_2$ by Bredig, Franck, and Fuldner in their original publication). This first, incorrect phase diagram by Bredig, Franck, and Fuldner emphasizes the reactivity of calcium orthophosphates with moisture at elevated temperatures. Examples of such high-temperature reactions are given below in equations which neglect the variable chemical composition of hydroxylapatite.

$$3\,Ca_4P_2O_9 + H_2O \longrightarrow 2\,Ca_5(OH)(PO_4)_3 + 2\,CaO \qquad (9\text{-}19)$$

$$3\,Ca_3(PO_4)_2 + CaO + H_2O \longrightarrow 2\,Ca_5(OH)(PO_4)_3 \qquad (9\text{-}20)$$

As would be expected from the phase diagram of Figure 9-22, hydroxylapatite when it is heated to a sufficiently high temperature (> about 1500°C.) will decompose into a mixture of true tricalcium phosphate plus tetracalcium phosphate (see below for $Ca_4P_2O_9$) This is shown for the hydroxylapatite for which the Ca/P mole ratio is $^5/_3$ in the following equation:

$$2\,Ca_5(OH)(PO_4)_3 \longrightarrow 2\,Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O \qquad (9\text{-}21)$$

Thermal studies such as the ones employed in outlining the orthophosphate end of the CaO–P_2O_5 phase diagram have shown that there is a true tricalcium orthophosphate which exhibits an x-ray pattern distinctly different from that of hydroxylapatite compositions. This true tricalcium phosphate exists in two crystalline forms[113]—a high-temperature form, α-$Ca_3(PO_4)_2$, and a low-temperature form, β-$Ca_3(PO_4)_2$, also known as whitlockite. The transition[112,114] between these two forms is somewhere in the neighborhood of 1100–1200°C. Because the transition is sluggish, both forms are to be found at room temperature, where the α-form is metastable. It should be noted that whitlockite appears in secondary geological formations which have probably not been subjected to temperatures sufficiently high to melt the calcium phosphates. This is in accord with the work of Perloff and Posner,[79] who recently made β-$Ca_3(PO_4)_2$ from aqueous solutions containing iron and chromium impurities at 300°C. under pressure.

There is also one other crystalline calcium orthophosphate in the CaO–P_2O_5 system. This is commonly called tetracalcium phosphate, or hilgen-

[113] For x-ray data on $Ca_3(PO_4)_2$, see A. L. Mackay, *Acta Cryst.*, **6**, 743 (1953) (α-variety); and A. L. Mackay, *ibid.*, **4**, 477 (1951); *ibid.*, **6**, 214 (1953) (β-variety).

[114] H. Schneiderhohn, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Dusseldorf*, **13**, 109 (1931); *Arch. Eisenhuttenw.*, **5**, 9 (1931)

stockite, and has the formula $Ca_4P_2O_9$, which may be rewritten as a double salt between tricalcium phosphate and lime, $Ca_3(PO_4)_2 \cdot CaO$. It should be noted that there is no oxyapatite, $Ca_{10}O(PO_4)_6$, in the phase diagram of Figure 9-22. If an oxyapatite really existed as a thermodynamically stable entity and dissolved congruently, it should appear on the phase diagram of Figure 9-22 at about the place where the eutectic between α-$Ca_3(PO_4)_2$ and $Ca_4P_2O_9$ is found. Trömel[111] carefully investigated the possibility of the existence of oxyapatite as a solid phase at temperatures below the liquidus region but could find no evidence of apatites at any temperature when water vapor was rigorously excluded from the ignitions.

The term "oxyapatite" occasionally appears in the literature concerned with precipitated calcium phosphates. The existence of this compound and its hydrates has been postulated to explain the variability of the hydroxylapatite composition which has been discussed in previous paragraphs. There seems to be no reason to assume that such a compound exists. Furthermore, crystallographic considerations[115] indicate that an oxygen atom cannot substitute for two hydroxyl groups in the apatite structure.

In Figure 9-23 phase diagrams are given[116] for the calcium orthophosphate systems involving fluoride, chloride, and carbonate ions. In these phase diagrams, fluorapatite and chlorapatite appear as distinct compounds. There is no carbonatapatite. However there are incongruent-melting compounds in both the $CaCO_3$–$Ca_3(PO_4)_2$ and $CaCl_2$–$Ca_3(PO_4)_2$ systems having compositions equivalent to a spodiosite, *i.e.*, $Ca_4CO_3(PO_4)_2$ and $Ca_4Cl_2(PO_4)_2$. It should be noted here that Nacken[116] has shown that there is a continuous series of solid solution from the fluorapatite to the chlorapatite.

The system CaO–P_2O_5–SiO_2 has been studied by several authors.[117] In addition to the usual calcium phosphates and calcium silicates, there are several mixed silicate-phosphates. The best established of these is silicocarnotite, $4\ CaO \cdot SiO_2 \cdot P_2O_5$, which is equivalent to the formula $Ca_4SiP_2O_{11}$. This salt melts around 1900°C.; and at normal temperatures in contact with water[118] converts very slowly to hydroxyapatite. Another

[115] D McConnell, *Am Mineralogist*, **22**, 977 (1937).

[116] R Nacken, *Zentr. Mineral. Geol.*, **1912**, 545 (fluorapatite and chlorapatite); W. Eitel, *Schriften konigsberg gelehrter Ges. Naturw. Kl.*, **1**, 159 (1924) (carbonate systems).

[117] R L. Barrett and W J. McCaughey, *Am. Mineralogist*, **27**, 680 (1942); G. Tromel, H. I Harkeort, and W. Hotop, *Z. anorg. Chem*, **256**, 253 (1948); G. Behrendt and H. Wentrup, *Arch. Eisenhuttenw.*, **7**, 95 (1933); O. Nielsen, *Ferrum*, **10**, 97 (1913); also see P. D S St. Pierre, *Can. Dept Mines and Tech. Surveys, Mines Branch, Tech. Paper No* **2**, 107 pp. (1953) for some work in the system $3\ CaO \cdot P_2O_5$–SiO_2–Al_2O_3.

[118] A. Schleede, W. Schmidt, and H. Kindt, *Z. Elektrochem.*, **38**, 633 (1932).

silicate-phosphate is nagelschmidite, 7 $CaO \cdot 2\ SiO_2 \cdot P_2O_5$, which is equivalent to $Ca_7Si_2P_2O_{16}$. Several other calcium silicate-phosphates have been suggested in the literature, but their existence is questionable.

A number of investigations have been carried out in Germany on the

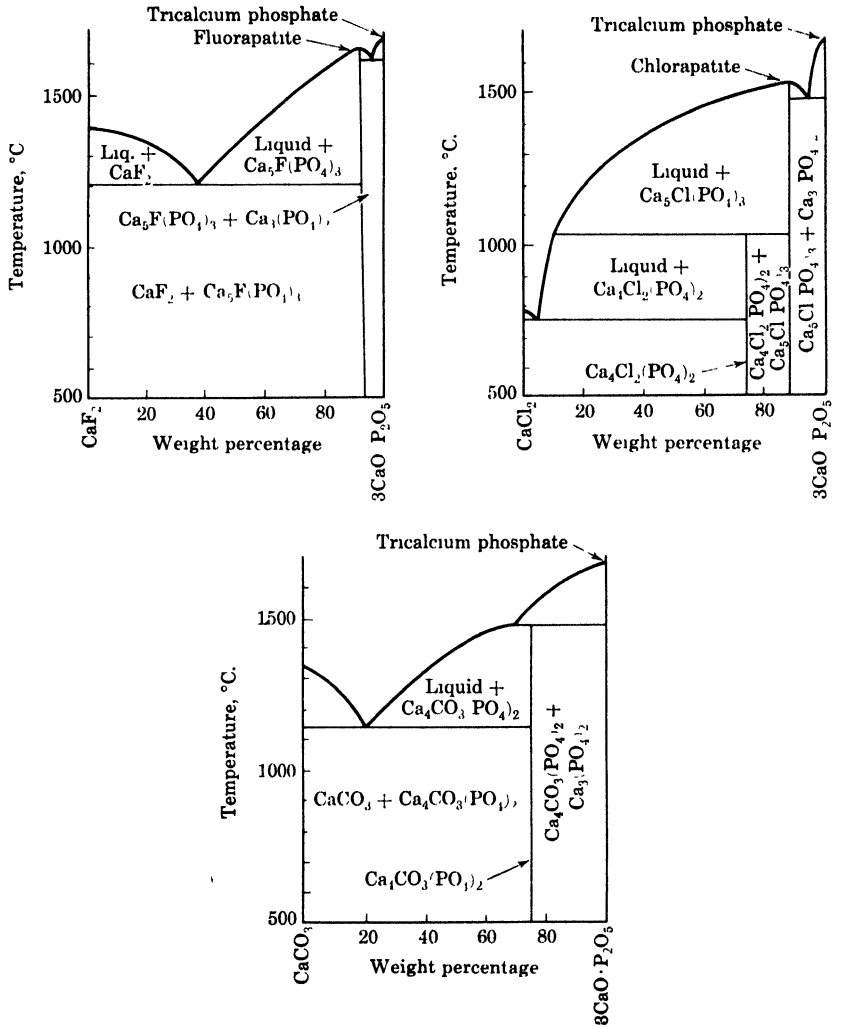


Fig. 9-23. Approximate phase diagrams of the systems CaF_2–$3CaO \cdot P_2O_5$, $CaCl_2$–$3CaO \cdot P_2O_5$, and $CaCO_3$–$3CaO \cdot P_2O_5$.

fundamental chemical relationships involved in the manufacture of iron.[11] In this work, studies have been carried out on such systems as $3\ CaO \cdot P_2O_5$–FeO, $3\ CaO \cdot P_2O_5$–CaF–FeO, and CaO–MnO–FeO–P_2O_5.

The Apatites

Over a century and a half ago, the name apatite was given to a group of minerals. This name, meaning deceiver (from ἀπατᾶν, to deceive), was given to the mineral because it was often confused with other minerals, such as aquamarine, amethyst, and olivine. The history of the investigations up to the present day concerned with this mineral show that the name was well chosen, as many persons who have studied the apatite minerals have surely been deceived by their findings.

Of all the phosphate minerals, the apatites are by far the most important. Thus, the major and practically only ore of phosphorus is fluorapatite, including the partially carbonated or hydroxylated varieties. Moreover, as has been previously pointed out, the hydroxylapatites, especially the carbonation variety, are of prime interest to biologists because they make up the mineral portion of teeth and bones in all animals. Due to the large variety of substitutions which are possible in their crystal structure, it is very difficult to write a general chemical formula for the apatites. However, the following formula is generally used. This formula, as given below, represents the unit cell of the $Ca_{10}F_2(PO_4)_6$ crystal which contains 42 atoms.

$$M_{10}X_2(RO_4)_6 \tag{9-22}$$

where M = Ca, Pb, Na, K, Sr, Mn, Zn, Cd, Mg, Fe″, Al, C (as CO_3), H_2O, and the rare earths (especially Ce); X = F, OH, Cl, Br, and, perhaps in certain cases, O;[120] and $RO_4 = PO_4$, AsO_4, VO_4, SO_4, and SiO_4.

In Table 9-4 a listing is given of the various apatites which have been described in the literature. Some of the names which have been given to naturally occurring apatite minerals but which are not accepted by Dana[121]

[119] For example, W. Oelsen and H. Maetz, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf*, **23**, No. 12, 195 (1941); W. Oelsen and H. Wiemer, *ibid.*, **24**, No. 13, 167 (1942); H. Wentrup, *Stahl u. Eisen*, **62**, 749 (1942); W. Krings, *Z. Metallkunde*, **26**, 247 (1934).

[120] There is no iodoapatite. For absence of I see E. Wilke-Dorfurt, J. Beck, and G. Plepp, *Z. anorg. u. allgem. Chem.*, **172**, 344 (1928). Although there is no oxyapatite as such, there may be a carbonate oxyapatite (dahllite), for remarks concerning which, see D. McConnell, *Am. J. Sci.*, **36**, 296 (1938).

[121] C. Palache, H. Berman, and C. Frondel, *Dana's System of Mineralogy*, 7th ed., John Wiley & Sons, Inc., New York, Vol. II, pp. 654–1016 (see pp. 877–906 for the apatite group).

are not presented in Table 9-4. Mineralogists have found that the naturally occurring apatites can be divided into two major groups: (1) the apatite series in which the dominant cation is calcium and (2) the pyromorphite series in which the dominant cation is lead. Generally speaking, it is observed that, in the naturally occurring minerals, lead does not substitute to a large amount for calcium in the apatite series, and calcium does not substitute in large amounts for lead in the pyromorphite series. However, complete substitution is observed in synthesized crystals. In the apatite series, silicon and sulfur substitute to some extent for phosphorus, but this

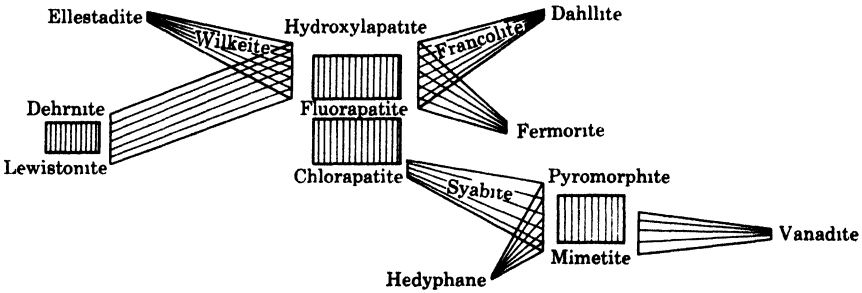


Fig. 9-24. Schematic diagram showing the solid solutions found between various naturally occurring apatite minerals The approximate chemical constitution of these minerals is given in Table 9-4.

substitution is considerably less in the pyromorphite series of related minerals. The pyromorphite series is marked by more or less complete replacements between arsenic, phosphorus, and vanadium, whereas arsenic and, especially, vanadium are usually not present in large amounts in the apatite series. In the pyromorphite series, chlorine is the major halide ion, as compared to the fluorine and hydroxyl ions in the apatite series.

These generalities can be directly related to ion size, with the larger ions being in the pyromorphite series. The unit cell dimensions in the apatite series are $a_0 \backsimeq 9.4$ and $c_0 \backsimeq 6.9$ A. as compared to $a_0 \backsimeq 10.0$ and $c_0 \backsimeq 7.3$ A. in the pyromorphite series. Intermediate members lying between the apatite and pyromorphite series will naturally exhibit intermediate unit cell dimensions.

All of the members of the apatite family (including the entire apatite and pyromorphite series) are related to each other by solid solutions. These relationships, as found in the naturally occurring apatites, are shown in Figure 9-24, where the apatite series appears at the center and left of the figure, and the pyromorphite series appears at the lower right.

TABLE 9-4
The Apatite Family[121,133]

Name	Generic formula	References	Remarks
	Naturally occurring		
Hydroxylapatite	$Ca_{10}(OH)_2(PO_4)_6$	121,73	Solid soln. with fluorapatite and francolite. Mn subst. for Ca
Fluorapatite	$Ca_{10}F_2(PO_4)_6$	121	Mn and Sr substs. for Ca. Cl and OH for F. Often considerable CO_2
Francolite	$(Ca, H_2O)_{10}(F, OH)_2(PO_4, CO_3)_6$	133	Intermediate between fluor or hydroxylapatite and dahllite
Dahllite	$[10\ CaO \cdot CO_2 \cdot 3\ P_2O_5 \cdot \psi\ H_2O]$	73,121	Carbonate-apatite. CO_2 does not subst. for F or OH
Wilkeite	$Ca_{10}(OH)_2(PO_4, SiO_4, SO_4)_6$	121	Intermediate between apatite and ellestadite
Ellestadite	$Ca_{10}(Cl, F, OH)_2(SiO_2, SO_4)_6$	121,122	PO_4^{3-} substituted by half SiO_2^- and half SO_3^{2-} to balance charge
Dehrnite	$(Ca, Na, K)_{10}(OH)_2(PO_4, CO_3)_6$	121	$K > Na$, K^+ for Ca^{2+} by using CO_3^{2-} for PO_4^{3-}
Lewistonite	$(Ca, K, Na, Al)_{10}(OH)_2(PO_4)_6$	121	$Na > K$, Na^+ and Al^{3+} apparently substs. for Ca^{2+}
Fermorite	$(Ca, Sr)_{10}(F, OH)_2(PO_4, AsO_4)_6$	121	Sr for Ca and As for P in the apatite structure
Chlorapatite	$Ca_{10}Cl_2(PO_4)_6$	121	Solid soln. with fluorapatite
Svabite	$(Ca, Pb)_{10}(F, Cl, OH)_2(AsO_4, PO_4)_6$	121	Pb for Ca up to ca. Pb/Ca = 1.4; P for As up to ca. 0.5 or more
Pyromorphite	$Pb_{10}Cl_2(PO_4, AsO_4)_6$	121	Solid soln. with mimetite; $P > As$. Ca substs. for Pb, also V for As
Mimetite	$Pb_{10}Cl_2(AsO_4, PO_4)_6$	121	$As > P$. As for pyromorphite
Hedyphane	$(Ca, Pb)_{10}Cl_2(AsO_4)_6$	121	Ca/P often close to 1. Solid soln. with mimetite

TABLE 9-4 (*continued*)

Name	Generic formula	References	Remarks
Vanadite	$Pb_{10}Cl_2(VO_4)_6$	121	Small amts. of Ca, Zn, and Cu for Pb, As for V up to As/V = 1:1
Britholite	$(Ca_4Al_6)F_2(SiO_4)_6$	123	Questionable odd example
Abukumalite	(Ca, Mn, Fe″, Mg)$_4$(Ce, V) $F_2(SiO_4, PO_4)_{2-3}$	124	Questionable odd example
	Some synthetic preparations		
Synth. hydroxylapatite	[13 CaO·4–5 H_2O·5 P_2O_5 up to 21 CaO·3–6H_2O·5P_2O_5]	73, also see text	Ca/P mole ratio varies from 1.3 to 2.1. See discussion of this in text
Mixed apatites	$Ca_{10}(F, OH, Cl)_2(PO_4)_6$	132	OH for Cl and for F. Cl/OH/F in all proportions
Strontium hydroxylapatite	$Sr_{10}(OH)_2(PO_4)_6$	126	
Cadmium hydroxylapatite	$Cd_{10}(OH)_2(PO_4)_6$	127	
Zinc hydroxylapatite	$Zn_{10}(OH)_2(PO_4)_6$	128	
Lead hydroxylapatite	$Pb_{10}(OH)_2(PO_4)_6$	128	
Synth. wilkeite	$Ca_{10}F_2(PO_4)_4(SiO_4)(SO_4)$	125, 122	Substs. SiO_4^{4-} + SO_4^{2-} for PO_4^{3-}
Sodium-calcium fluoride-phosphate-sulfates	$(Na_2Ca_8)F_2(PO_4)_4(SO_4)_2$ $(Na_4Ca_6)F_2(PO_4)_2(SO_4)_4$	125	Ca_3PO_4–$CaSO_4$–Na_2SO_4–CaF_2 mixed salts
Sodium fluorapatite (?)	$Ca_9NaF(PO_4)_6$	131	
Sodium chlorapatite (?)	$Ca_9NaCl(PO_4)_6$	131	
Chromium in apatites	$(Ca, Na)_{10}(F, OH)_2(PO_4, CrO_4)_6$	130	Up to several % Cr, fraction % Na_2O
Chlorapatite containing rare earths	$(Ca, Ce, Di, Yt)_{10}F_2(PO_4)^{6+}$	129	Up to 13% $CePO_4$, 3% $DiPO_4$, and 6% $YtPO_4$ in the chlorapatite
Lanthanum oxyapatite	$Ca_8La_2O_2(PO_4)_6$	129	

All of the members of the apatite series exhibit hexagonal crystals, belonging to the hexagonal-dipyramidal class-6/m-(space group, $C6_3/m$). The earliest x-ray structure determinations in the apatite family were carried out on fluorapatite by Mehmel and Náray-Szabó.[134] The structures of these two authors differ in that Mehmel gives positions 000 and $00^1/_2$ for the two fluorine atoms, as compared to the positions $00^1/_4$, $00^3/_4$ given by Náray-Szabó. Although the choice between the two structures for fluorapatite is difficult to make, later authors[135,136] have accepted and improved upon the Náray-Szabó structure for fluorapatite. According to Hendricks *et al.*,[135] pyromorphite, mimetite, vanadinite, and chlorapatite have crystal structures similar to that suggested by Mehmel, whereas fluorapatite and hydroxylapatite have the Náray-Szabô structure. However, the existence of a continuous solid solution between fluorapatite and chlorapatite indicates that the two structures are sufficiently similar that a discontinuity between them is not necessary.

The problem of the structure of carbonate-bearing apatites is one which has received considerable attention. In the original empirical picture set up to describe the apatites, it was supposed that the carbonate substituted for hydroxyl or fluoride ion, but this idea is incompatible with the x-ray structure. At the present time, two explanations for the inclusion of car-

[122] R. Klement, *Naturwiss.*, **27**, 57 (1939); R. Klement and P. Dihn, *ibid.*, **29**, 301 (1941).

[123] G. Hägele and F. Machatschki, *Naturwiss.*, **27**, 132 (1939).

[124] F. Machatschki, *Zentr. Mineral. Geol., Abt. A.*, **1939**, 161

[125] P. Dihn and R. Klement, *Z. Elektrochem.*, **48**, 331 (1942).

[126] R. Klement, *Z. anorg. u. allgem. Chem.*, **242**, 215 (1939).

[127] R. Klement and F. Zureda, *Z. anorg. u. allgem. Chem.*, **245**, 229 (1940)

[128] W. Rathje, *Ber.*, **74B**, 342, 357 (1941). F. Zambonini and A. Ferrari, *Atti accad Lincei*, **7**, 283 (1928).

[129] F. Zambonini, *Z. Krist. Festband P. v. Groth*, **58**, 226 (1923).

[130] C. Minguzzi, *Periodico mineral. (Rome)*, **12**, 343 (1941).

[131] L. H. Borgström, *Finska Kemistsamfundets Medd.*, **40**, 51 (1931), *ibid.*, **41**, 116 (1932).

[132] R. Wallaeys and G. Chaudron, *Compt. rend.*, **230**, 1867 (1950); *ibid.*, **231**, 355 (1950); R. Wallaeys, *Ann. chim. (Paris)*, **7**, 808 (1952).

[133] D. McConnell, *Am. Mineralogist*, **23**, 1 (1938).

[134] M. Mehmel, *Z. Krist.*, **75**, 323 (1930); St. Náray-Szabó, *ibid.*, **75**, 387 (1930); also see H. Hentschel, *Zentr. Mineral. Geol.*, **1923**, 609 for a Laue x-ray study.

[135] S. B. Hendricks, M. E. Jefferson, and V. M. Mosley, *Z. Krist.*, **81**, 352 (1932).

[136] C. A. Beevers and D. B. McIntyre, *Mineral. Mag.*, **27**, 254 (1946); W. F. Bale, *Am. J. Roentgenol. Radium Therapy*, **43**, 735 (1940); also see A. S. Posner and S. R. Stephenson, *J. Dental Research*, **31**, 371 (1952) and H. Brasseur, *Bull. classe sci. Acad. roy. Belg.*, **36**, 521 (1950).

bonate in the apatites have been proposed. One of these explanations, which has primarily been directed to the state of carbon dioxide in bone mineral, is based on the idea that carbonate and, perhaps, bicarbonate[137] ions are sorbed on the surface primarily by exchange with phosphate.[73] Thus, when a finely crystalline synthetic apatite is equilibrated with a carbonate solution, it is found that the amount of CO_2 taken up by the apatite is proportional to the mole ratio CO_2/P_2O_5 in solution.[138] Likewise, the CO_2 can be nearly completely removed from carbonate-bearing apatites by acid-leaching without affecting the x-ray pattern.[139] Also, the infrared pattern in carbonate-bearing apatite exhibits the two important bands of calcite.[139] The other explanation,[140] which has been primarily directed toward the structure of francolite, involves substitutions throughout the crystal lattice. In developing this explanation, McConnell assumes that water molecules replace calcium ions in the apatite structure in order that the planar carbonate ion may replace the tetrahedral PO_4 groups in the structure and yet keep the positive and negative charges balanced.

A number of authors, other than the ones quoted here, have studied the problem of carbonate-bearing apatites, and the majority of them have used either the adsorption or crystalline solid solution hypotheses which are discussed above. However, some of these authors have concluded that the carbonate-bearing apatites are simple admixtures of calcium carbonate with hydroxyl- or fluorapatites. If this is the case, the particles of calcium carbonate must be extremely small and/or amorphous, since the x-ray patterns of the carbonate-bearing apatites usually show no evidence of crystalline carbonates, although the CO_2 is present in sufficiently large quantities to give good calcite or aragonite diffraction lines. In essence, this means that the carbonate is probably sorbed on the apatite crystallites. At present, this sorption theory appears to give the best explanation of the known facts.

As has been stated previously,[73] the Ca/P mole ratio in precipitated

[137] Fragmentary evidence that some of the carbon dioxide may be present as bicarbonate ion is given by W. F. Neuman, M. W. Neuman, E. R. Main, J. O'Leary, and F. A. Smith, *J. Biol. Chem.*, **187**, 655 (1950).

[138] W. F. Neuman, *Atomic Energy Report UR-238*, 1953; A. E. Sobel, A. Hanok, H. A Kirshner, and I. Fankuchen, *J. Dental Research*, **28**, 61 (1949).

[139] A. S. Posner and G. Duyckaerts, *Experientia*, **10**, 424 (1954); A. Posner, *Norelco Reporter*, **2**, No. 2, 26 (1955).

[140] D. McConnell, *Bull. soc. franç. mineral. et crist.*, **75**, 429 (1952); J. W. Gruner and D. McConnell, *Z. Krist.*, **97A**, 208 (1937); also see E. B. Sandell, M. H. Hey, and D. McConnell, *Mineralog. Mag.*, **25**, 395 (1939); D. McConnell, *J. Dental Research*, **31**, 53 (1952); *J. Wash. Acad. Sci.*, **42**, No. 2, 36 (1952).

hydroxylapatites can range from about 1.4 to 2.0. In other words, any unignited calcium phosphate having a composition within 20% of that corresponding to the Ca/P ratio of 1.67 for the formula $Ca_{10}(OH)_2(PO_4)_6$ is hydroxylapatite! Although such ranges in composition (crystalline solid solutions, with the term "solid solution" used in a broad, empirical sense) are well known in mineralogy—so well known, in fact, that mineralogists accept them as obvious without needing individual explanations—a great deal of the study of hydroxylapatite has been carried out by inorganic and biological chemists who were shocked at finding a crystalline compound with so much variability in composition. Even in very recent times, there are some scientists[141] in this field of study who call the hydroxylapatite for which Ca/P = 1.5 "α-tricalcium phosphate." The main justification for this terminology appears to be the fact that hydroxylapatite approximating the formula $Ca_5OH(PO_4)_3$ is unaffected by heating, whereas the precipitated "α-tricalcium phosphate" is converted into true tricalcium phosphate upon strong heating. However, such behavior is to be expected on the basis of the phase diagram studies of the $CaO–P_2O_5$ system in the presence[112] and absence[111,112] of moisture. The results of such ignition studies depend only on the CaO/P_2O_5 ratio and not on the atomic arrangement in the unignited structure.[76]

The early chemical papers on the calcium phosphates usually divide the basic calcium phosphates into the categories of hydroxylapatite and tricalcium phosphate on the basis of proximate chemical analysis alone. When the fact that a large range of compositions all give the same x-ray diffraction pattern became better known, it was assumed that hydroxylapatite adsorbed phosphate ions on its surface in order to give a Ca/P mole ratio lower than 1.67 and adsorbed calcium ions in order to give higher mole ratios. If the term "adsorption" is restricted to mean only a loose type of sorption, this conclusion is definitely untrue because of the following points: (1) The tiny crystals of the finest precipitated hydroxylapatite for which Ca/P = 1.50 would have to adsorb as much as one phosphate ion for every four in the crystal, which would indicate an absurdly thick adsorption layer. (2) Crystal growth[142] of an hydroxylapatite having a Ca/P mole ratio of 1.5 in a hydrothermal bomb to give microscopic crystals did not lead to

[141] See M. J. Dallemagne, H. Brasseur, and J. Melon, *Bull. soc. chim. France*, **1949**, Mises au point D 138–45; *ibid.*, **3–4**, 138 (1949); *Bull. soc. chim. biol.*, **31**, 425 (1949); M. J. Dallemagne and H. Brasseur, *Experientia*, **3**, 469 (1947); H. A. L. Brasseur, *International Union Pure Applied Chemistry, Colloquium of Section for Inorganic Chemistry Münster*, **2–6 Sept. 1954**, Verlag Chemie Weinheim, Germany, 1954, p. 199.

[142] A. S. Posner and S. R. Stephenson, *J. Dental Research*, **31**, 371 (1952); also see ref. 141.

desorption of any phosphate ion, since no phosphorus was detected in the bomb water. (3) A final argument against loosely adsorbed phosphate ions in hydroxylapatites having "low" Ca/P ratios is given by a study of the exchange of calcium and phosphorus by use of radioactive tracer techniques.[143] It was found that the ratio of calcium exchange to phosphorus exchange was the same for two different hydroxylapatities having Ca/P mole ratios of 1.50 and 1.66, respectively.

A related explanation for the variable composition of hydroxylapatite which undoubtedly must play some role in the true picture is surface substitutions[73] on the tiny crystallites. A detailed calculation based on measured surface area indicates that this hypothesis can completely explain the data in the case of one hydroxylapatite (Ca/P = 1.5) which was critically studied. In this calculation, an isomorphic substitution of hydronium ion for calcium ion was postulated in surface positions. Such a substitution can explain the existence of precipitates with Ca/P mole ratios varying from 1.4 to 1.8.

Explanations of the variability of hydroxylapatites have also been based on the idea of isomorphic substitutions involving the entire crystal. Most of these explanations have not gone into structural details. For example, it is postulated that there may be "a statistical absence of calcium ions from structural positions, probably supplanted in some way by hydrogen ions for electrical neutrality."[144] In the only detailed applications[145] of the isomorphic substitution theory to hydroxylapatite, it is proposed that water and hydrogen ion be substituted for calcium within the unit cell, with differences in the calcium content of the crystal being related to index of refraction and x-ray data.

There is no doubt that isomorphic substitution, both at the surface and within the crystal, is the principal reason why variable composition is encountered with hydroxylapatites. Probably in any particular case, the over-all composition is partially due to surface substitution and partially to substitution throughout the crystal. In view of the many kinds of substitutions which are possible in the apatite series, it seems quite probable that any given over-all composition will turn out to be attributable to a number of substitution mechanisms (some of which may not have as yet

[143] J. H. Weikel and W. F. Neuman, *U. S. Atomic Energy Rept. UR-228*, 1952.

[144] A. S. Posner, *International Union Pure Applied Chemistry, Colloquium of Section for Inorganic Chemistry Münster, 2–6 Sept. 1954*, Verlag Chemie, Weinheim, Germany, 1954, p. 207.

[145] P. W. Arnold, *Trans. Faraday Soc.*, **46**, 1061 (1950); A. S. Posner and A. Perloff, *J. Research Natl. Bur. Standards*, **58**, 279 (1957).

even been postulated) taking place in the unit cell—which, it must be remembered, has 42 atomic positions.

It seems very probable that the measured variability of composition of precipitated hydroxylapatites is due to both sorption and substitution of atoms within the crystal lattice. Experiments supporting the sorption (surface layer) hypothesis have been reported by Mattson,[107] and a brief recent review of work supporting the isomorphic substitution hypothesis is given by Posner *et al.*[116]

OTHER INORGANIC PHOSPHATES

Magnesium Orthophosphates

The chemistry of the magnesium orthophosphates is very similar to that of the calcium orthophosphates, except that the question of the composition of more basic magnesium phosphates has not been as carefully resolved as in the case of calcium. The phase diagram[147] of the MgO–H_2O–P_2O_5 orthophosphate system is given in Figure 9-25. Comparison of this system to the calcium system shows that magnesium gives somewhat greater solubility. Thus, at 25°C. the saturated solution in contact with the monobasic and dibasic salts (the most concentrated solution with respect to both the alkaline earth metal and the phosphate ions) contains 8.3 wt.-% MgO and 33.1 wt.-% P_2O_5 in the magnesium system as compared to 5.785 wt.-% CaO and 24.10 wt.-% P_2O_5 in the calcium system.

Mono- and dimagnesium orthophosphates decompose in contact with water to form free phosphoric acid and a more alkaline phosphate in essentially the same manner as the calcium phosphates.[148] Trimagnesium phosphate has been described[149] in the literature and is probably best known as its octahydrate, bobierrite.[150] In addition, a 22-hydrate has been described by several authors. Solubility studies indicate that the trimagnesium phosphate has a slightly higher solubility in water than does the hydroxylapatite corresponding to the tricalcium phosphate composition.[151] As in the case

[146] A. S. Posner, C. Fabry, and M. J. Dallemagne, *Biochim. et Biophys. Acta*, **15**, 304 (1954).

[147] A. P. Belopol'skii, S. Ya. Shpunt, M. N. Shul'gina, *J. Applied Chem. (U.S.S.R.)*, **23**, 823 (1950).

[148] F. K. Cameron and J. M. Bell, *J. Phys. Chem.*, **11**, 363 (1907).

[149] W. Rathje, *Naturwiss.*, **29**, 221 (1941); A. N. Agte, P. A. Arkhangel'skii, and N. I. Birger, *J. Gen. Chem. (U.S.S.R.)*, **10**, 295 (1940); H. Bassett and W. L. Bedwell, *J. Chem. Soc.*, **1933**, 854, 871, 877; C. Zinzadzé, *Compt. rend.*, **194**, 1498 (1932); N. S. Kurnakov and I. A. Andreevskii, *Ann. inst. anal. phys.-chim. (U.S.S.R.)*, **2**, 485 (1924)

[150] R. Klement, *Z. anorg. u. allgem. Chem.*, **228**, 232 (1936).

[151] F. Mach and P. Lederle, *Phosphorsäure*, **2**, 469 (1932); M. von Wrangell and E Koch, *Landwistach. Jahrb.*, **63**, 677 (1926).

of precipitated hydroxylapatites in the calcium series, "trimagnesium phosphate" forms a solid solution on the basic side, giving similar x-ray diffraction patterns for varying MgO/P_2O_5 ratios. However, both the trimagnesium salt and its more basic solid solution crystallize in the monoclinic system and therefore cannot be called apatites as has been done by several authors.

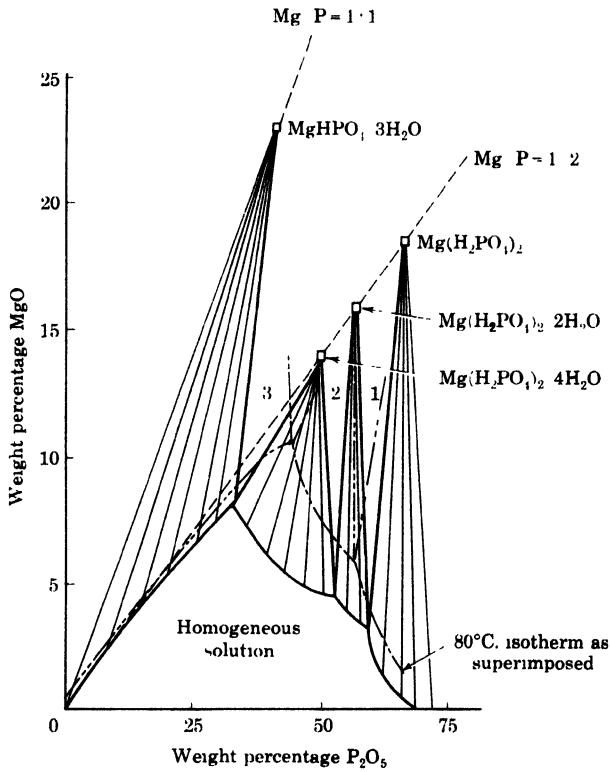


Fig. 9-25. The system $MgO–H_2O–P_2O_5$ for the magnesium orthophosphates at 25°C. (The 80°C. isotherm, in which only $MgHPO_4 \cdot 3H_2O$, $Mg(H_2PO_4) \cdot 2H_2O$, and anhydrous $Mg(H_2PO_4)_2$ appear, is superimposed.) The three-phase areas in the 25°C. isotherm are numbered.

Klement[150] has named the alkaline magnesium salt "hydroxyl-bobierrite." Optical and x-ray data show that hydroxyl-bobierrite is crystallographically identical to trimagnesium phosphate, so that the similarity between the calcium and magnesium systems appears to be very close although, of course, the bobierrites are monoclinic as compared to the hexagonal apa-

tites. Klement has further shown that continued hydrolysis of $MgHPO_4$ finally leads to hydrated magnesium oxide. There may be a crystalline species between hydroxyl-bobierrite and hydrated magnesium oxide which is different than either. As is the case with the apatites, hydroxyl-bobierrite crystallizes very slowly[152] and is usually obtained as extremely fine crystals.

A magnesium fluoride-phosphate, $Mg_2F(PO_4)$, named wagnerite, is the basis of a complicated series of solid solutions—a series which appears to be somewhat similar in complexity to the apatite series. Examples of compounds[153] exhibiting the wagnerite structure are $LiMg_3F_2(PO_4)(SO_4)$ and $NaMg_3F_2(PO_4)(SO_4)$. The chemically equivalent calcium compound, $Ca_2Cl(PO_4)$, exhibits a different x-ray powder pattern and cannot be called a wagnerite. It may, however, be isomorphous with the rare Swedish mineral spodiosite, which is assigned the formula, $Ca_2F(PO_4)$.

Orthophosphates of Alkali and Doubly Charged Metal Ions

There are a number of mixed salts involving the orthophosphate ion, one of the alkali metal ions, and a doubly charged metal ion such as the alkaline earth metals. These salts, which have been known for over a century,[154] are all quite insoluble in water. For example, magnesium ammonium phosphate, $NH_4MgPO_4 \cdot 6\ H_2O$, is soluble in water to the extent of 0.0987 g./l. at 25°C. The solubility of this salt is increased by the presence of ammonium chloride and decreased by ammonium hydroxide, so that at 25°C. there is 0.3452 g./l. dissolved in 1 *N* NH_4Cl and 0.0090 g./l. dissolved in 5 *N* NH_4OH. In a mixture containing 1 *N* NH_4Cl and 5 *N* NH_4OH, the solubility of $NH_4MgPO_4 \cdot 6\ H_2O$ is 0.0248 g./l.

This salt, magnesium ammonium phosphate, is a common precipitate used in the analysis of phosphorus.[155] By means of this precipitate, phosphorus can be separated from[156] Fe^{3+}, Al, Ti, Zr, Zn, Se, Te, Mo, W, Sn, and Ca. A highly precise gravimetric procedure for phosphorus is based on the precipitation of this salt, followed by ignition to magnesium pyrophosphate, $Mg_2P_2O_7$. When this procedure is carried out properly,[156]

[152] W. Rathje, *Ber.*, **74B**, 546 (1941).

[153] R. Klement and F. Gembruch, *Naturwiss.*, **29**, 301 (1941); R. Klement and P Dihn, *Z. anorg. u. allgem. Chem.*, **240**, 31 (1938).

[154] H. Rose, *Ann. Physik.*, **77**, 292 (1849).

[155] R. Klement, *Handbuch der Analytischen Chemie*, eds. W. Fresenius and G. Jander, Springer, Berlin, 1953, Vol. Vaβ, "Phosphor" ($MgNH_4PO_4 \cdot 6\ H_2O$ on pp. 118–29; phosphomolybdates on pp. 30–117).

[156] E. Karl-Kroupa, J. R. Van Wazer, and C. H. Russell, *Scott's Standard Methods of Chemical Analysis*, ed. N. H. Furman, 6th ed., D. Van Nostrand Co., Inc., New York (manuscript submitted).

TABLE 9-5
Orthophosphates of Alkali Metals with Doubly Charged Metal Ions

Salt	References	Preparation[a]	Remarks
$LiCaPO_4$	154	S	
$Na_3MgH(PO_4)_2$	157	S	
$NaCaPO_4$	154, 161, 163, 166	T	High-temperature form = hexagonal Low-temperature form = rhombic
$NaSrPO_4$	163, 164	T	High-temperature form = tetragonal Low-temperature form = hexagonal
$NaSrPO_4 \cdot 18\ H_2O$	167	S	
$NaBaPO_4$	154, 163	S, T	High-temperature form = tetragonal Low-temperature form = rhombic (?)
$Na_9Cu_5H_2(PO_4)_7$	157	S	
$NaZnPO_4$	157	S	
$NaZnPO_4 \cdot ca\ 1\ H_2O$	157	S	
$NaCdPO_4$	157	S	
$Na_{7-9}Cd_{5-7}H(PO_4)_{6-8}$	157	S	A solid solution within range given
$Na_3MnH(PO_4)_2$	157	S	A solid solution of $NaMnPO_4$ and Na_2HPO_4
$Na_4Co_3H_2(PO_4)_4 \cdot 8\ H_2O$	157	S	
$NaNiPO_4 \cdot 7\ H_2O$	157	S	
$KCaPO_4$	154, 163, 164	S, T	Same form at high and low temperatures = hexagonal
$KSrPO_4$	154, 163, 164	S, T	High-temperature form = tetragonal Low-temperature form = hexagonal
$KBaPO_4$	154, 163, 164	T	High-temperature form = tetragonal Low-temperature form = rhombic
$KBaPO_4 \cdot 10\ H_2O$	165, 167	S	
$KZnPO_4$	163	T	
NH_4BePO_4	152	T	
NH_4MgPO_4	158	T	Heating of monohydrate in NH_3 at 160°C.
$NH_4MgPO_4 \cdot H_2O$	158	T	Heating of hexahydrate in NH_3
$NH_4MgPO_4 \cdot 6\ H_2O$	155, 158, 162	S	Used in analysis of P
$NH_4CaPO_4 \cdot 7\ H_2O$	158, 165	S	
$NH_4BaPO_4 \cdot 7\ H_2O$	158	S	
$NH_4CuPO_4 \cdot H_2O$	158	T	By heating following complex
$(NH_4)_4[Cu(NH_3)_2](PO_4)_2 \cdot 7\ H_2O$	158	S	From strongly ammoniacal solutions

[a] S = from solution; T = thermally.

an absolute accuracy of ±0.05% can be obtained in the proximate analysis of phosphorus. In the process of igniting magnesium ammonium phosphate to magnesium pyrophosphate, the precipitate has been noticed to

glow very brightly. This incandescence has been the subject of some study and theorization[157,158] but is well worth additional investigation with modern techniques, such as x-ray diffraction and paper chromatography.

It has been known for a long time[154] that extended washing of the orthophosphates of alkali metal ions plus doubly charged metal ions leads to decomposition. As might be expected, leaching with hot water speeds this process, which results in an apatite or normal phosphate of the doubly charged metal. The ammonium derivatives tend to lose both water and ammonia to a dry atmosphere at relatively low temperatures.[158,159] This decomposition can be inhibited by water and ammonia vapors. A listing of a number of orthophosphates of ammonia or alkali metal ions with doubly charged metal ions is given in Table 9-5. Details concerning the individual salts can be found in the references listed in the table. It is interesting to note that NH_4MgPO_4 forms a peroxidate salt with H_2O_2.[160]

Phosphate Minerals

Several hundred different names for phosphate minerals have been employed in the literature. However, only 187 of these named minerals have been accepted for inclusion in Dana's System of Mineralogy,[121] since a number of phosphate minerals bearing different names have been found to be identical. Nearly all of these 187 accepted minerals are well-crystallized substances on which crystal parameters have been obtained. Some of these data—along with other information primarily of chemical interest—are given in Appendix A, in which are listed all of these accepted minerals and several rare minerals not given in Dana. For more details the reader is referred to Dana.

[157] H. Bassett and W. L. Bedwell, *J. Chem. Soc.*, **1933**, 854; Z. Karaoglanow and P. Dimitrow, *Z. anal. Chem.*, **57**, 353 (1918).

[158] V. Auger and N. Ivanoff, *Compt. rend.*, **204**, 434 (1937).

[159] S. J. Kiehl and H. B. Hardt, *J. Am. Chem. Soc.*, **55**, 605 (1933) (dissociation pressures); C. Duval, *Chim. anal.*, **31**, 173 (1949) (thermobalance studies).

[160] F. Munzberg, *Lotos*, **76**, 351 (1928).

[161] P. Blanc, *Bull. soc. chim. France*, **1952**, 205.

[162] A. Travers and Mlle. Perron, *Ann. chim.*, **1**, No. 10, 298 (1924).

[163] R. Klement and F. Steckenreiter, *Z. anorg. u. allgem. Chem.*, **245**, 12 (1940); R. Klement and R. Uffelmann, *Naturwiss.*, **29**, 300 (1941).

[164] L. V. R. Ouvrard, *Ann. Chim. Phys.*, **16**, No. 6, 297 (1889); *Compt. rend.*, **106**, 1599 (1888).

[165] A. de Schulten, *Compt. rend.*, **96**, 706 (1883); *Bull. soc. min.*, **27**, 97 (1904); *Bull. soc. chim.*, **39**, No. 2, 500 (1883).

[166] H. Rose, *Ann. Physik.*, **95**, 437 (1855).

[167] A. Joly, *Compt. rend.*, **104**, 1702 (1887).

Many of the phosphate minerals contain a considerable number of different atoms in their structure. Some of these minerals are alleged to have extremely big units cells, although it should be noted that the use of unnecessarily large unit cells (which are multiples of the real unit cell) has plagued the mineralogical literature. Thus, for example, arrojadite, $Na_{24}(Fe'', Mn'')_{60}(PO_4)_{48}$, is assigned a unit cell containing 324 atoms! The dimensions of this cell are $a_0 = 16.6$ A., $b_0 = 10.0$ A, $c_0 = 24.0$ A., and $\beta = 93°37'$.

Solid solutions and isomorphic substitutions occur very generally in the mineralogy of the phosphates. Nearly all of the crystalline phosphates listed in Dana exhibit more or less substitution in their crystal lattices. Substitution of adjacent elements in a given period of the periodic table is extremely common Thus, PO_4 groups are often replaced wholly or in part by AsO_4 groups; and, calcium, strontium, and barium (or magnesium, calcium, and strontium) often substitute for each other. Similarly, sodium and potassium appear interchangeably in many orthophosphate minerals. In addition, there are more complicated substitutions, such as replacement of calcium by sodium or by cerium with a concomitant addition or deletion of hydrogen or replacement in the anions in order to keep the over-all charge balanced.

As pointed out in the above paragraph, a given phosphate mineral may correspond to a considerable range of chemical composition. In addition, isomorphism (in the broad sense) between different phosphate minerals and between phosphate, arsenate, sulfate, and silicate minerals is quite common. The term "isomorphism" has been used very loosely in the scientific literature to cover both (1) mixed-crystal formation (stereochemical miscibility or crystalline solid-solutions) and (2) close crystallographic relationships (isotypism or isostructural relationships) as demonstrated by identical, or nearly identical, space groups and nearly equivalent crystal parameters, such as unit-cell dimensions. Before the advent of x-ray diffraction, close crystallographic relationships were determined by careful study of crystal shapes. Hence, the generic term "isomorphism" (same shape), which was at first limited to isostructural relationships and later was extended so as to include crystalline solid solutions. In the late 19th century "isomorphism" became quite synonymous with the formation of crystalline solid solutions and has often been restricted to this meaning. In this text, the terms "solid solution" and "mixed crystals" are used interchangeably as opposed to "isostructural relationships."

The distinction between mixed-crystal formation and an isostructural relationship is quite arbitrary, because it depends on existing knowledge of

TABLE 9-6
Isomorphism in the Orthophosphate Minerals
(Crystalline solid solutions and isostructural crystals)

Names	Generic base formulas	Type of isomorphism	Crystal class and space group	Unit-cell dimensions a_0	b_0	c_0	Atoms per unit cell
			Monoclinic				
Brushite	$CaHPO_4 \cdot 2\,H_2O$		A2	5 88	15 15	6 37	52
Pharmacolite	$CaH\,AsO_4\ 2\,H_2O$	Isostructural, also		6 00	15 40	6 29	52
Ardealite	$Ca_2H(PO_4)(SO_4) \cdot 4\,H_2O$	closely related to	—	5 67	14 64	6 28	50
Churchite	$(Ce, Ca)PO_4 \cdot 2\,H_2O$	gypsum through	—	5 46	15 12	6 28	48
Weinschenkite	$(Y, Er)PO_4 \cdot 2\,H_2O$	ardealite	P2/a	5 46	15 12	6.28	48
			Monoclinic				
Weinschenkite	$(Y, Er)PO_4 \cdot 2\,H_2O$	Isostructural, also closely related to	P2/a	6 48	15 12	6 28	48
Gypsum	$CaSO_4\ 2\,H_2O$	brushite series	P2/a	5 67	15 15	6 28	48
			Monoclinic				
Phosphorresslerite	$MgH\,PO_4\ 7\,H_2O$	Isostructural	—	—	—	—	224(?)
Roesslerite	$MgHAsO_4 \cdot 7\,H_2O$		A2/a	11 4	25 4	6 60	224
			Hexagonal				
Whitlockite	$Ca_3(PO_4)_2$	Isostructural	R3c	2(5 16)	—	2(18 5)	91 in full (2x) cell
Palmerite	$K_2Pb(SO_4)_2$		R3m	5 58	—	20 7	13
			Tetragonal				
Bobierrite	$Mg_3(PO_4)_2\ 8\,H_2O$		$P2_1/c$	9 95	2(6 9)	4 64	74
Hoernesite	$Mg_3(AsO_4)_2 \cdot 8\,H_2O$			—	-	--	74(?)

			Monoclinic				
Triploidite	$Mn_2(PO_4)(OH)$	Phosphates form solid solutions. The arsenate is isostructural and may form solid solutions with the others	$P2_1/a$	12 3	13 4	9.9	144
Wolfeite	$Fe_2''(PO_4)(OH)$		$P2_1/a$	12 1	13 1	9 7	144
Sarkinite	$Mn_2(AsO_4)(OH)$		$C2_1/a$	12 7	13 5	10 2	144
			Orthorhombic				
Olivenite	$Cu_2(AsO_4)(OH)$	Isostructural. Partial solid solution between olivenite and libenthenite	Pnnm	8 16	8 54	5 86	36
Libenthenite	$Cu_2(PO_4)(OH)$		Pnnm	8 08	8 43	5 90	36
Adamite	$Zn_2(AsO_4)(OH)$		Pnnm	8 30	8 51	6 04	36
Andalusite	$Al_2(SiO_4)(OH)$						
			Monoclinic				
Herderite	$CaBe(PO_4)F$	Isotructural Probably complete solid solution between herderite and hydroxylherderite	$P2_1/c$	- -	-	-	32
Hydroxylherderite	$CaBe(PO_4)OH$		$P2_1/c$	4 80	7 68	9 80	32
Datolith	$Ca\,B(SO_4)OH$		$P2_1/c$	4 82	7 62	9 84	32
			Orthorhombic				
Triphylite	$LiFe''PO_4$	Isostructural	Pnma	6 05	10 4	4 75	28
Lithiophilite	$Li\,Mn''PO_4$		Pnma	6 00	10 3	4 65	28
			Hexagonal				
Ferric phosphate	$Fe'''PO_4$	Aluminum phosphate forms solid solution with arsenate All isostructural	$C/3_12$	—	—	—	—
Berlinite	$AlPO_4$		$C/3_12$	4 93	—	10 94	18
Quartz	SiO_2 [*i.e.*, $Si(SiO_4)$]		$C/3_12$	4 90		2(5 39)	2(9)
Aluminum arsenate	$Al\,AsO_4$		$C/3_12$	—	—	—	18

(*continued*)

TABLE 9-6 (*continued*)

Names	Generic base formulas	Type of isomorphism	Crystal class and space group	Unit-cell dimensions a_0	b_0	c_0	Atoms per unit cell
			Tetragonal?				
Boron phosphate	BPO_4	Isostructural. Probably solid solution between the boron arsenate and phosphate		4.33		6 64	
Low cristobalite	SiO_2			4 96		6 92	
Boron arsenate	$BAsO_4$						
			Orthorhombic				
Heterosite	$Fe'''PO_4$	Isostructural	—	5 8	9 7	4 8	24
Purpurite	$Mn\,PO_4$		—	—	—	—	
			Orthorhombic				
Variscite	$AlPO_4 \cdot 2\,H_2O$	All isostructural. Phosphates form solid solutions between themselves as do arsenates	P cab	9 85	9 55	8 50	89
Strengite	$Fe'''PO_4 \cdot 2\,H_2O$		P cab	10 1	9 80	8 65	89
Mansfieldite	$AlAsO_4 \cdot 2\,H_2O$		P cab	—	—	—	89
Scorodite	$Fe'''AsO_4 \cdot 2\,H_2O$		P cab	10 3	10.0	8 92	89
Norbergite	$Mg_3(OH, F)_2SiO_4$		P mcn	10 2	2(4 70)	8 72	
			Monoclinic				
Metastrengite	$Fe'''PO_4 \cdot 2\,H_2O$	Partially isostructural	P $2_1/n$	5 28	9 75	8 71	48
Metavariscite	$AlPO_4 \cdot 2\,H_2O$		P $2_1/n$	5 28	9 75	8 71	48
Phosphophyllite	$Zn_2(Fe'',Mn)(PO_4)_2 \cdot 4H_2O$		P $2_1/c$	10 2	5 08	10 5	50
			Orthorhombic				
Reddingite	$Mn_3(PO_4)_2\,3\,H_2O$	Isostructural					
Phosphoferrite	$Fe_3''(PO_4)_2\,3\,H_2O$		P mna	9 52	10 1	8 70	88

			Monoclinic				
Vivianite	$Fe_3''(PO_4)_2\ 8\ H_2O$	All isostructural. Anna-	C 2/m	10 0	13 4	4 69	74
Annabergite	$Ni_3(AsO_4)_2 \cdot 8\ H_2O$	bergite, erythrite, and	C 2/m	10 1	13 3	5 00	74
Erythrite	$Co_3(AsO_4)_2 \cdot 8\ H_2O$	koettigite prob. form	C 2/m	10 2	13 3	4 73	74
Koettigite	$Zn_3(AsO_4)_2 \cdot 8\ H_2O$	solid solutions as well		10 1	13 3	4 70	74
			Tetragonal				
Xenotime	$Y\ PO_4$	Isostructural Also	14/and	6 88	—	6 03	24
Zircon	$ZrSiO_4$	closely related to the	14/and	6 58	—	5 93	24
Calcium chromate	$CaCrO_4$	monazite group	14/and				24
Yttrium vanadate	$Y\ VO_4$		14/and				24
			Monoclinic				
Monazite	$(Ce, La, Y, Th)\ PO_4$	Isostructural. Closely	$P2_1/n$	6 78	6 99	6 45	24
Crocoite	$PbCrO_4$	related to the xeno-	$P2_1/n$	7 10	7 40	6 80	24
Strontium chromate	$SrCrO_4$	time group	$P2_1/n$				24
Bismuth phosphate	$BiPO_4$		$P2_1/n$	6 74	6 95	6 41	24
			Orthorhombic				
Ferri-sicklerite	$(LiFe''')\ PO_4$	Isostructural	—	5 9	10 0	4 7	24
Sicklerite	$(LiMn)\ PO_4$		—	6 2(?)	10 4(?)	5 0(?)	24
Alluaudite	$(NaFe''')\ PO_4$	Isostructural	?	—	—	—	?
Mangan-alluaudite	$(NaMn)\ PO_4$			—	—	—	
			Orthorhombic				
Huhnerkobelite	$(Na, Ca)\ Fe_2''(PO_4)_2$	Isostructural	—	—	—	—	?
Varulite	$(Na, Ca)Mn_2\ (PO_4)_2$		—	—	—	—	?
			Monoclinic				
Beryllonite	$NaBePO_4$	Isostructural	$P\ 2_1/c$	2(813)	7.76	2(14 1)	4(84)
Trimerite	$CaMn_2Be_3(SiO_4)_3$		$P\ 2_1/c$	16 1	7 60	27 9	336

(*continued*)

TABLE 9-6 (*continued*)

Names	Generic base formulas	Type of isomorphism	Crystal class and space group	Unit-cell dimensions a_0	b_0	c_0	Atoms per unit cell
			Cubic				
Griphite	$(Na, Ca, Fe, Al)_6Mn_4(PO_4)_5(OH, F)_8$	Isostructural	Ia3d	12.3	—	—	ca. 160
Grossularite	$Ca_3(Al, Fe''')_2(SiO_4)_3$		Ia3d	11.8	—	—	160
Andradite	$Ca_3Al_2(SiO_4)_3$		Ia3d	12.0	—	—	160
Magnesium berzeliite	$(Ca, Na)_3(Mg, Mn)_2(AsO_4)_3$		Ia3d	12.3	—	—	160
Manganese berzeliite	$(Ca,Na)_3(Mn, Mg)_2(AsO_4)_3$		Ia3d	12.5	—	—	160
			Triclinic				
Amblygonite	$(Li,Na)Al(PO_4)F$	Solid solutions	P1	5.18	7.11	5.03	16
Montebrasite	$(Li,Na)Al(PO_4)(OH)$						
Natronmontebrasite	$(Na,Li)Al(PO_4)(OH, F)$						
			Orthorhombic(?)				
Andrewsite	$Cu_3Fe_6''''(PO_4)_4(OH)_{12}$	Isostructural and perhaps form solid solutions	?	?	?	?	
Laubmanite	$Fe_3''Fe_6'''(PO_4)_4(OH)_{12}$						
			Hexagonal				
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$	Isostructural. Alunite and natroalunite also form solid solutions					27(?)
Gorceixite	$BaAl_3(PO_4)_2(OH)_5 \cdot H_2O$						27(?)
Goyazite	$SrAl_3(PO_4)_2(OH)_5 \cdot H_2O$		$R\bar{3}m$	6.97	—	16.5	27
Crandollite	$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$						
Deltaite	$Ca_2Al_3(PO_4)_2(OH)_4 \cdot H_2O$		$R\bar{3}m$	6.98	—	16.1	25
Florencite	$CeAl_3(PO_4)_2(OH)_6$						27(?)
Dussertite	$BaFe_3'''(AsO_4)_2(OH)_5 \cdot H_2O$						28(?)

Alunite	$KAl_3(SO_4)_2(OH)_6$		R3m	6 96		17 4	26
Natroalunite	$NaAl_3(SO_4)_2(OH)_6$						26(?)
Beudantite	$PbFe_3'''(AsO_4)(SO_4)(OH)_6$						26(?)
Corkite	$PbFe_3'''(PO_4)(SO_4)(OH)_6$						26(?)
Hinsdalite	(Pb, Sr) $Al_3(PO_4)(SO_4)(OH)_6$						26(?)
Svanbergite	$SrAl_3(PO_4)(SO_4)(OH)_6$		R$\bar{3}$m	6 99	--	16.8	26
Woodhouseite	$CaAl_3(PO_4)(SO_4)(OH)_6$		R$\bar{3}$m	6 96		16 3	26
Jarosite	$KFe_3'''(SO_4)_2(OH)_6$		R3m	7 20	- -	17 0	26
Ammoniojarosite	$(NH_4)Fe_3'''(SO_4)_2(OH)_6$		R3m	7 20		17 0	26
Natrojarosite	$NaFe_3'''(SO_4)_2(OH)_6$		R3m	7 18		16 3	26
Argentojarosite	$AgFe_3'''(SO_4)_2(OH)_6$		R3m	7 22		16 4	26
			Orthorhombic				
Frondelite	$MnFe_4'''(PO_4)_3(OH)_5$	Solid solution	B 22_12 or	13 9	17 0	5 21	120
Rockbridgeite	$Fe_4'''(PO_4)_3(OH)_5$		B 22_12				
			Monoclinic				
Lazulite	$MgAl_2(PO_4)_2(OH)_2$	Solid solution	P $2_1/n$	7 12	7 24	7 10	34
Scorzalite	$Fe''Al_2(PO_4)_2(OH)_2$		P $2_1/n$	7 15	7 32	7 14	34
			Triclinic				
Turquoise	$CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$	Solid solution	P$\bar{1}$	7 47	9 93	7 67	55
Chalcosiderite	$CuFe_6'''(PO_4)_4(OH)_8 \cdot 4H_2O$		P$\bar{1}$	7 66	10.18	7 88	55
			Tetragonal				
Torbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 8\text{–}12\ H_2O$	Isostructural	I 4/mmm	7 05	—	20 5	82–106
Autunite	$Ca(UO_2)_2(PO_4)_2$ 10–12 H_2O		I 4/mmm	6 99	—	20 6	94–106
Uranocircite	$Ba(UO_2)_2(PO_4)_2 \cdot$ ca. $8H_2O$			—	—	—	ca. 82(?)
Saléeite	$Mg(UO_2)_2(PO_4)_2 \cdot 10\ H_2O$		I 4/mmm	6 98	—	19 8	94(?)
Zeunerite	$Cu(UO_2)_2(AsO_4)_2 \cdot 10\text{–}16\ H_2O$			-	—	—	94 130
Uranospinite	$Ca(UO_2)_2(AsO_4)_2 \cdot 8\ H_2O$			—	—	—	82(?)
			Tetragonal				
Metatorbernite	$Cu(UO_2)_2(PO_4)_2 \cdot 8\ H_2O$	Isostructural. (Similar	P4/nmm	6 95	—	8 60	41
Meta-autunite-II	$Ca(UO_2)_2(PO_4)_2 \cdot 2.6\ H_2O$	to the torbernite	P4/nmm	6 98	—	8 42	23–35
Meta-autunite	$Ca(UO_2)_2(PO_4)_2 \cdot 8\ H_2O$	group of minerals)		7 13	—	8 83	41

the mutual relationships of the compounds in question. Often compounds which are isostructural are shown by later studies to form solid solutions as well. On the other hand, there are a few cases of anomalous mixed crystal formation[168] in which the crystallographic relationships between the end members of the solid solution are not at all apparent from the crystal parameters.

In Table 9-6 the major examples of isomorphism[169] in the orthophosphate minerals are presented. In some complicated structures, such as the series headed by the mineral plumbogummite, there is an extreme amount of substitution. The apatites, which have been discussed in considerable detail in previous paragraphs, are another example (see Table 9-4) to show how complicated the solid solutions and various substitutions can be. The phosphate minerals are extremely interesting, in that they demonstrate how complicated the chemistry of the "simple" orthophosphate ion can become. Presumably, complicated crystal structures involving a large number of different substitutable anions and cations, such as are found in the orthophosphate minerals, can also occur in the chain and ring phosphates, as well as for the lower oxyacids of phosphorus.

Mineralogists have perforce taken up the study of crystals in which there is a large amount of isomorphic substitution because such crystals commonly occur in nature. Chemists, however, have shied away from study of these systems, probably in great part because chemical terminology is very inadequate in describing them.

Covalent-Network Type of Orthophosphates

X-ray studies of a number of orthophosphates have shown that the cations, with the exception of hydrogen, have a large coordination number, as is usually expected for a positively charged ion in a crystal. Thus, the coordination number of potassium and other alkali metals in their orthophosphate crystals is eight. Calcium in anhydrous dicalcium phosphate exhibits two coordination numbers, seven in the case of calcium in one crystallographic position and eight in the case of the calcium in another

[168] See W. Hückel, *Structural Chemistry of Inorganic Compounds* (translated from the German by L. H. Long), Elsevier Publishing Co., Amsterdam, 1951, Vol. II, pp. 713–18; see pp. 690–737 for a thorough discussion of isomorphism.

[169] For a thorough review of isomorphism in the phosphates, see W. Kleber and B. Winkhaus, *Fortschr. Mineral.*, **28**, 175 (1949).

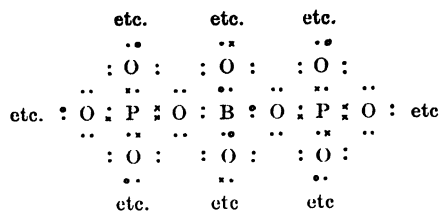
position. In the apatites, calcium has a coordination number of six as has the metal ion in anhydrous indium and thallic phosphates, $InPO_4$ and $TlPO_4$. In cerous phosphate,[170] $CePO_4$, and the related phosphates of other rare earths, the rare earth metal ion is coordinated to eight oxygen atoms.

A preliminary study[171] of synthetically prepared crystals of autunite, $Ca(UO_2)_2(PO_4)_2 \cdot n\,H_2O$, and related minerals (metaautunite, the barium derivative, etc.) has shown that the uranium atoms are each surrounded by six oxygen atoms, and that the crystals are composed of sheets formed by PO_4 tetrahedra and UO_6 octahedra linked together by the sharing of a single oxygen atom between polyhedra. Large cavities exist between the sheets, and these cavities are filled by hydrated calcium ions which appear to be quite free to move around between the uranium phosphate sheets. In this structure both the uranium and calcium ions exhibit the large coordination number of a cation, although it could well be argued that this compound is a calcium uranophosphate in which the uranium as a d^2sp^3-hybrid is bonded into a complex anion. In all of the structures mentioned above, the phosphorus has a coordination number of four and hence must be in sp^3-hybridization. The P-O distance in all cases is close to 1.55 A.

On the other hand, a very different type of crystal structure is found in the case of boron phosphate, BPO_4,[172] aluminum phosphate, $AlPO_4$,[173] and ferric phosphate, $FePO_4$.[174] In these crystals, which are isostructural with one or more forms of SiO_2, not only is the phosphorus surrounded by a tetrahedron of oxygen atoms, but so are the boron, aluminum, and iron atoms, respectively. In other words, these crystals are more properly thought of as mixed anhydrides of P_2O_5 and alumina or P_2O_5 and boria than as aluminum or boron salts of orthophosphoric acid. They are discussed under orthophosphates, however, since PO_4 groups isolated from each other are involved.

In the crystal of BPO_4 (equivalent to $B_2O_3 \cdot P_2O_5$), the P-O distance was found[172] to be equal to 1.55 A. and the B-O distance 1.44 A. In $BAsO_4$, which is isostructural with the boron phosphate, the B-O distance is a little larger, being equal to 1.49 A. A reasonable picture of the structure is as follows: By sharing electrons as shown on the next page

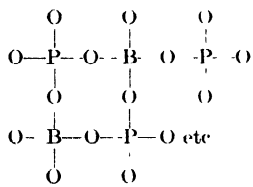
[170] R. C. L. Mooney, *Acta Cryst.*, **3**, 337 (1950); *ibid.*, **9**, 113 (1956).
[171] J. Beintema, *Rec. trav. chim.*, **57**, 155 (1938).
[172] G. E. R. Schulze, *Z. physik. Chem.*, **B24**, 215 (1934).
[173] H. Strunz, *Z. Krist.*, **103**, 228 (1941).
[174] V. Caglioti, *Atti accad. Lincei*, **22**, 146 (1935).



(9-23)

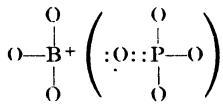
where × = electron donated by P, ○ = electron donated by B, and • = electron donated by O, all electrons being truly equivalent.

the boron and phosphorus atoms (each in sp^3-hybridization) can thus be represented as being connected by means of σ-bonds (single bonds) to the four oxygen atoms tetrahedrally surrounding each of them. A portion of such a crystal is pictured below in a two-dimensional projection by the usual single-connection notation.



(9-24A)

The P-O distance of 1.55 A., however, corresponds to about $^1/_3$ π-bond per σ-bond, according to the discussion given on pp. 36–43. This can be accounted for by a mechanism such as the one shown below in which the boron atom receives a positive charge and the PO_4 group receives a negative charge which is undoubtedly located on the oxygen atoms



(9-24B)

Such a mechanism allows π-bonding in the PO_4 group. Although the σ-bond contribution made by boron to a bond length is not so well known as the phosphorus contribution (see Chapt. 2), it appears that the measured B-O bond length of 1.44 A. may be slightly smaller than would be expected for a boron-oxygen σ-bond.[175] Although it would be possible to

[175] L. Pauling, *The Nature of the Chemical Bond*, 2nd ed., Cornell University Press, Ithaca, N. Y., 1948, p. 164 gives a single bond radius for boron of 0.88 A., which leads to a B-O single bond length uncorrected for electronegativity effects of 1.5 A. In the borates, bond distances of about 1.36 A. are usually found (*e.g.*, see W. H. Zachariasen, *Z. Krist.*, **88**, 150 (1934) and *J. Chem. Phys.*, **5**, 919 (1937) for B-O distance in orthoboric acid and sodium and potassium metaborates, respectively). It should be remembered that boron exhibits the planar sp^2-hybridization in the borates so that a third *p*-orbital is available for π-bonding.

conceive of a similar but considerably smaller π-bond shortening of the B-O interatomic distance such as was described for the P—O bond, this does not seem very probable because of the high energy involved in using the *d*-orbitals of first-row elements such as boron. The possible shortening of the B-O interatomic distance as compared to a summed B—O σ-bond must therefore be mainly attributed to a combination of covalent bonding

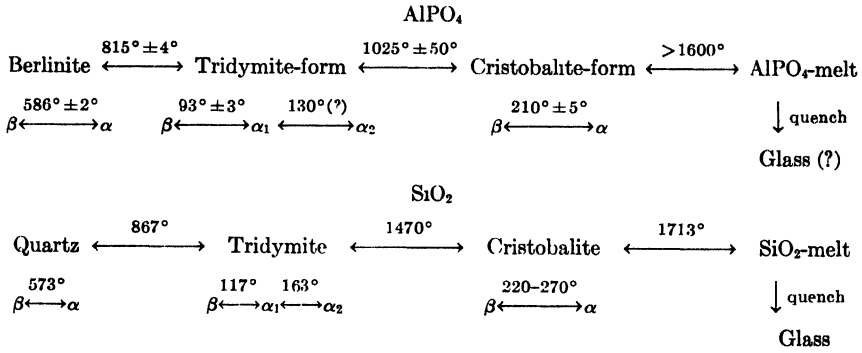


Fig. 9-26. Transitions in crystalline trialuminum phosphate as compared to those in the completely isostructural silicon dioxide.

with the coulombic attraction between the positively charged boron and the surrounding oxygens which bear part of a negative charge. It should be noted that the P—O π-bonding and the concomitant positive charging of the boron atoms with distributed negative charging of the oxygen atoms is superimposed upon the basic σ-bond structure shown above in structure 9-24.

As might be expected, boron phosphate is an unusually stable substance. Thus, although neither B_2O_3 nor P_2O_5 is very refractory, even in their polymerized forms, boron phosphate does not exhibit an appreciable rate of vaporization[176] until temperatures above about 1450°C. are reached. Moreover, boron phosphate must have a relatively low free energy, as it is the stable form over a very large area of the ternary system B_2O_3–P_2O_5–SiO_2,[177] and it can also be precipitated from aqueous solution.[178] With respect to interactions between borates and phosphates, it is interesting to note that there is some evidence for the existence of borophosphate ions in

[176] F. A. Hummel and T. A. Kupinski, *J. Am. Chem. Soc.*, **72**, 5318 (1950).

[177] W. J. Englert and F. A. Hummel, *J. Soc. Glass Technol.*, **39**, 121 (1955); also see *ibid.*, **39**, 113 (1955).

[178] M. Levi and L. F. Gilbert, *J. Chem. Soc.*, **1927**, 2117.

concentrated aqueous solution.[179] Such ions are probably structurally related to the B—O—P network found in boron orthophosphate.

As previously stated, the crystal structure of BPO_4 is similar to that of SiO_2, in that the crystal is recognized as a distorted, high-cristobalite type. However, the isostructural relationships[180] between $AlPO_4$ and SiO_2 are much closer, with a direct parallelism between all of the seven crystalline modifications of SiO_2 and similar modifications of $AlPO_4$. As shown in Figure 9-26, the transition temperatures are somewhat lower for $AlPO_4$ than for SiO_2. Not only are the equivalent forms similar, but the inversions from one form to another also show a distinct parallelism. Thus, the transformations back and forth from quartz to tridymite to crystobalite are sluggish and exhibit hysteresis effects, whereas the high-low inversions, which do not involve major structural rearrangements, take place readily. Similar results are found for transformations between the equivalent forms of $AlPO_4$. It appears that the parallelism between $AlPO_4$ and SiO_2 continues into the melt to some extent,[181] and that $Al_2O_3 \cdot P_2O_5$ glasses can be made. However, there is a paper which claims that this is not so.[182] The latter paper claims that melts in the Na_2O–($AlPO_4 \cdot P_2O_5$) system are much less viscous than equivalent melts in the Na_2O–SiO_2 system at the same temperature.

In the investigations concerned with the similarity between $AlPO_4$ and SiO_2, it has often been pointed out that the radius and electron requirements of substituting silicon atoms by aluminum and phosphorus are admirably balanced.

Since study of the parallelism between $AlPO_4$ and SiO_2 has been carried out in laboratories primarily devoted to crystallography and mineralogy, the jargon of these disciplines has been used in much of the literature. That is to say, the discussions have been couched in terms of hypothetical Al^{3+}, Si^{4+}, and P^{5+} ions so dear to the heart of the crystallographer.

Thus, aluminum has one less electron than silicon and phosphorus has one more. In addition, the aluminum radius is larger than that of silicon by about the same amount as the silicon radius is larger than that of phos-

[179] G. R. Levi, A. Aguzzi, and R. Sannicolò, *Gazz. chim. ital.*, **68**, 179 (1938); G. R. Levi and R. Curti, *ibid.*, **68**, 376 (1938).

[180] B. Winkhaus, "Die kistallchemischen Bezeihungen zwischen Aluminomorthophosphat $AlPO_4$ und Silicumdioxyd SiO_2," Doctoral Dissertation, Bonn, 1951; W. R. Beck, *J. Am. Ceramic Soc.*, **32**, 157 (1949); F. A. Hummel, *ibid.*, **32**, 320 (1949) and others. For a review, see ref. 169.

[181] F. Drexler and W. Schütz, *Glastech. Ber.*, **24**, 172 (1951).

[182] A. Dietzel and H. J. Poegel, *Naturwiss.*, **40**, 604 (1953).

phorus (see Fig. 2-3 on p. 27). In a recent partial structure study,[183] it was pointed out that the intensity of the reflection of x-rays from the basal plane (0003) of $AlPO_4$ is almost completely caused by oxygen atoms, with the contributions of Al and P practically cancelling out each other. This behavior is to be expected from the general type of electronic structure which was described above for boron orthophosphate. In addition, in the case of aluminum orthophosphate, there is the added possibility of some π-bonding between the aluminum and oxygen atoms, since the *d*-orbitals of aluminum as a second-row atom are reasonably available for bond formation. There should not be so much π-bonding to aluminum as to phosphorus in the aluminum phosphates, however, since aluminum has a considerably lower electronegativity than does phosphorus (see Fig. 2-2 on p. 24).

Silver orthophosphate,[184] Ag_3PO_4, is similar to the boron, aluminum, and iron phosphates, in that each silver atom has only four oxygen atoms as nearest neighbors (Ag-O = 2.34 A.), but, in addition, two similar silver atoms are rather close to each of these silver atoms (Ag-Ag = 3.00 A. as compared to 2.88 A. in metallic silver). The P-O separation is also unusually large, being quoted at 1.61 A. ± 0.03 A. This distance corresponds to about 0.2 π-bond per σ-bond as compared to the average value of 0.4 π-bond per σ-bond for the P–O bond in other phosphates.

Trisilver orthophosphate, Ag_3PO_4, gives considerable evidence of its unusual structure. For one thing, it has a yellow color, although most silver salts and most phosphates are colorless. Moreover, it appears to give an extremely broad absorption peak[185] at 1200 $cm.^{-1}$ in the infrared without showing the usual fine structure common to most phosphates. This indicates a large amount of mechanical coupling between the constituent atoms.

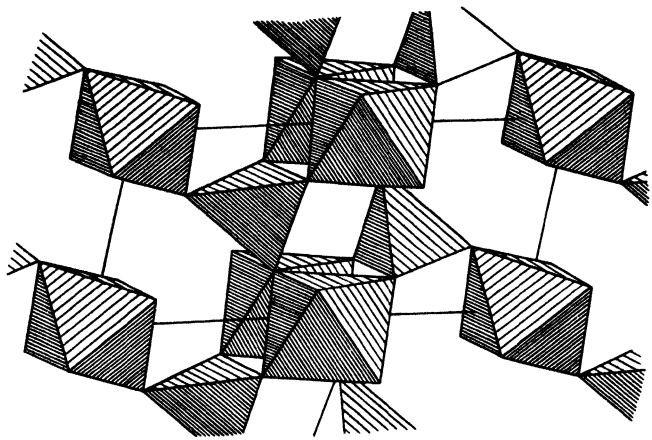
Another orthophosphate exhibiting[186] unusually long P-O distances is vivianite, $Fe_3(PO_4)_2 \cdot 8\,H_2O$. As expected, the phosphorus atoms are tetrahedrally surrounded by oxygen atoms, and the iron atoms are octahedrally surrounded by the oxygens of the PO_4 groups and of the water molecules. There are complex bands of interconnected phosphorus tetrahedra and iron octahedra extending throughout the crystal, with individual bands apparently being held together only by hydrogen bonding between the water groups. Structure (9-25) is a representation of such a band.

[183] R. Brill and A. P. De Bretteville, *Acta Cryst.*, **8**, 567 (1955); *Am. Mineralogist*, **33**, 750 (1948). The use of ions in the text of these papers should be ignored.

[184] L. Helmholz, *J. Chem. Phys.*, **4**, 316 (1936).

[185] M A Stock and J R Van Wazer, unpublished results at the Monsanto Chemical Co

[186] H. Mori and T Ito, *Acta Cryst.*, **3**, 1 (1950).



(9-25)

It should be noted that the unshared corners of the FeO_6 octahedra correspond to oxygen atoms from water groups, with the hydrogens not being shown. There are two types of octahedra—a single FeO_6 group (or more properly an $O_2Fe(OH_2)_4$ group) and a double group, Fe_2O_{10} or $O_6Fe_2(OH_2)_4$. The P-O distance to the oxygen atom of a PO_4 group shared with the single $O_2Fe(OH_2)_4$ group is 1.57 A., a normal distance corresponding to 0.3 π-bonds per σ-bond, whereas the P-O distance to the oxygen atom shared between the phosphorus and the two iron atoms of the $O_6Fe_2(OH_2)_4$ double group is 1.62 A. The P-O distances between a given phosphorus and the two separate corners of the $O_6Fe_2(OH_2)_4$ double group are each 1.68 A., a distance corresponding to essentially no π-bonding. It is apparent from these data that vivianite represents a transition from the three-dimensional mixed polymer to a simple orthophosphate based on isolated PO_4 groups. Although vivianite is based on a six-fold coordination of iron, the relatively small amount (0.5) of π-bonding per PO_4 group and its unbalanced distribution indicate that the iron must exhibit some covalent bonding (as a d^2sp^3 hybrid), probably with considerable ionic character.

Orthophosphate Complexes in Solution

The complexing of transition metals by orthophosphates has been known for a long time. As early as 1882, the decolorizing action of orthophosphoric acid on ferric iron was utilized in analytical procedures.[187] In addi-

[187] A Weller, *Berliner Ber.*, **15**, 25, 92 (1882), also see C. Rhinehart, *Stahl u. Eisen*, **4**, 709 (1884), *Chem Ztg.*, **13**, 323 (1889).

tion to this decolorizing action, there is considerably more evidence to indicate the existence of orthophosphato-ferric complexes. Thus, the oxidation potential of the ferrous-ferric system is lowered in the presence of orthophosphoric acid, and the conductivity of mixtures of phosphoric acid and ferric salts is found to be higher[188] than the sum of the separate conductivities. In transference-number experiments, it has been shown[189] that ferric ion in the presence of excess orthophosphoric acid moves toward the anode.

A number of different formulations of orthophosphato-ferric complexes have been suggested. In the presence of chloride ion, the complex has been said[188] to contain three chlorine atoms and one PO_4 group per iron atom. However, the solubility of $FePO_4$ in acid solutions containing chloride or phosphate rises with increase in the phosphate concentration but is independent of the concentration of chloride ion[190] as would be expected for a complex containing no chloride. Ion exchange experiments[191] indicate the presence in solution of a complex containing three orthophosphate groups per iron atom. On the other hand, conductometric titration curves of phosphoric acid with ferric chloride have been interpreted[192] to show the existence of both $Fe(HPO_4)^+$ and $Fe(HPO_4)_2^-$ ions. The relative stability of the orthophosphate complexes of ferric iron as compared to ferric complexes with other anions has been studied[193] using spectral measurements.

Several salts of the phosphato-ferric acids have been isolated[194] in crystalline form. In these salts, two anions have been found. They are the di- and triorthophosphato-ferrate ions, $[Fe(PO_4)_2]^{3-}$ and $[Fe(PO_4)_3]^{2-}$.

Aluminum acts similarly to iron in that it is strongly complexed by orthophosphoric acid.[188,190] The dissociation constants of aluminum complexes with orthophosphoric acid have been reported in terms of several assumed formulas for the complexes.[195] In addition, the probable existence of complexes of orthophosphate ion has been reported for a number of metal ions,

[188] S. R. Carter and H. F. Clews, *J. Chem. Soc.*, **125**, 1880 (1924); L. Dede, *Z. anorg. u allgem. Chem.*, **125**, 28 (1923).

[189] R. W. Atteberry, unpublished findings at the Monsanto Chemical Co.

[190] K. A. Jensen, *Z. anorg. u. allgem. Chem.*, **221**, 1 (1934).

[191] J. E. Salmon, *J. Chem. Soc.*, **1952**, 2316.

[192] S. Banerjee, *J. Indian Chem. Soc.*, **27**, 417 (1950).

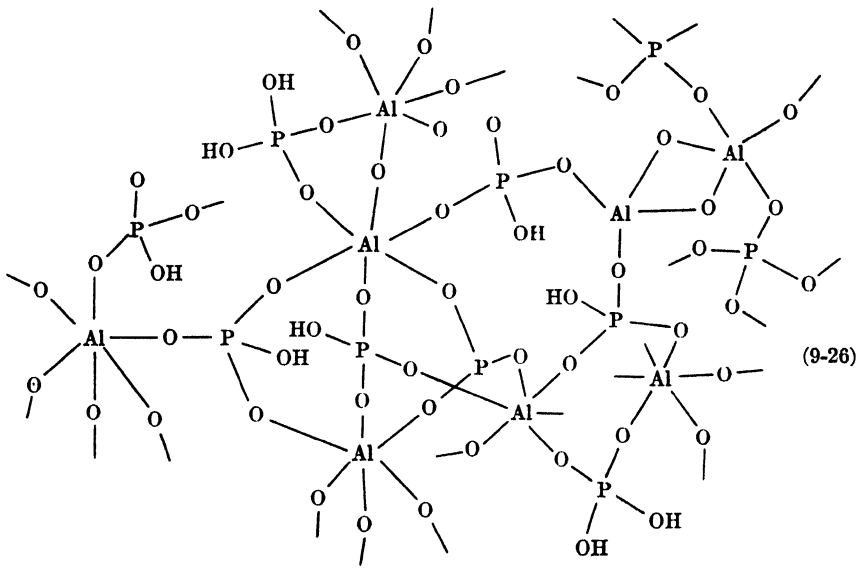
[193] D. D. Thoms and E. S. Gantz, *Proc. Indiana Acad. Sci.*, **56**, 130 (1946).

[194] R. F. Weinland and F. Ensgraber, *Z. anorg. Chem.*, **84**, 340 (1914); A. Sanfourché and B. Focet, *Compt. rend.*, **195**, 873 (1932); also see A. Bailer, *Das ternare System Ferriphosphate-Phosphorsaure-Wasser und die Phosphatoferrisauren*, Thesis, Univ. of Stuttgart, 1930, 68 pp.

[195] N. Bjerrum and C. R. Dahm, *Z. physik. Chem., Bodenstein-Festband*, **627** (1931)

including cobalt,[196] copper,[197] silver,[198] thorium,[199] plutonium,[200] uranium,[201] and even calcium.[97]

When approximately 1.0–1.5 mole of Al_2O_3 per mole of P_2O_5 is dissolved in orthophosphoric acid, there results an extremely viscous fluid which can be dried down to an amorphous solid.[202] This amorphous material can be dispersed in water to form again viscous, adhesive solutions. It is believed[203] that these solutions consist of aggregation polymers in which interactions between the aluminum ions and the orthophosphate ions lead to three-dimensional networks such as the one indicated below.



(9-26)

The stability and degree of polymerization of these aluminum phosphate aggregation polymers are greatly dependent on the pH of the medium,

[196] C. Duval, *Compt. rend.*, **224**, 1362 (1947).

[197] J. Mercadie, *Compt. rend.*, **221**, 581 (1945).

[198] H. C. Saraswat, *Proc. Indian Acad. Sci.*, **30A**, 329 (1949).

[199] E. L. Zabroski, H. W. Alter, and F. K. Heumann, *J. Am. Chem. Soc.*, **73**, 5646 (1951).

[200] E. L. King, AECD-2521 (CN-3360), Oct. 1945, Declass. Mar. 1949, *Nuclear Sci. Absts.*, **2**, 330 (1949).

[201] A. L. Dounce, J. F. Flagg, P. E. Fanta, G. H. Tishkoff, T. H. Lan, and M. Kaley, *Natl. Nuclear Energy Ser., Manhattan Project Tech. Sect. Div. VI, I, Pt. I*, 55 (1949).

[202] H. H. Greger, U. S. Pat. 2,460,344 (Feb. 1, 1949); Brit. Pat. 597,169 (Jan. 20 1948); *Brick and Clay Record*, **117**, No. 2, 63, 68 (1950).

[203] C. F. Callis, J. R Van Wazer, and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954).

probably in much the same way as is found for the isopoly and heteropoly acids of the chromates, tungstates, and vanadates (see the immediately following sections of this chapter). With the present limited amount of information which is available concerning the aluminum orthophosphate aggregation polymers, these materials can be considered as being similar to the heteropoly acids, and, at the same time, they can be classified as complexes between aluminum and orthophosphate ions in concentrated solution. Indeed, it is quite possible that these aggregation polymers represent a transition between the two cases of (1) heteropoly acids and (2) soluble complexes—both of which, although they usually have been treated as separate phenomena, are obviously related.

Solubility and vapor pressure data have been interpreted to substantiate the existence of borophosphoric acids in concentrated solution.[178,179] Solids exhibiting the composition of salts of borophosphoric acid have been prepared;[204] and the mineral lüneburgite—which has been made in the laboratory[205] and has the formula $3\ MgO \cdot B_2O_3 \cdot P_2O_5 \cdot 8\ H_2O$—may be a borophosphate, although the boron and phosphorus atoms are probably in separate oxyanions.

HETEROPOLY ACIDS OF PHOSPHORUS

Introduction to Heteropoly Acids of Phosphorus

The elements of Subgroups V and VI in the periodic table exhibit a pronounced tendency to form condensed (or poly) acids as the pH is lowered in solutions containing simple anions based on these elements. These are the isopoly acids, which are well known in the case of vanadium, chromium, molybdenum, and tungsten. When other acid anions such as phosphate, silicate, and borate are also present in the solution, the heterpoly acids are formed as the pH is decreased. Many of the heteropoly acids and their salts readily give large crystals in which there are a number of moles of MoO_3, WO_3, or V_2O_5 per mole of, for example, P_2O_5, SiO_2, or B_2O_3. In addition, the salts contain several moles of metal ion per mole of, say, P_2O_5; and both the acids and their salts crystallize with a large number of moles of water per mole of P_2O_5. These heteropoly acids were first discovered by Berzelius[206] in 1817 and have been of considerable interest to chemists ever

[204] D. Ghiron and D. Grischott, *Atti accad. Lincei*, **20**, 391 (1934); D. Ghiron, *Atti. congr. nazl. chim. pura ed applicata, Rome, 5th Congr.*, **1935**, Pt. 1, 366 (1936).

[205] W. Berdesinski, *Naturwiss.*, **38**, 476 (1951).

[206] J. J. Berzelius, *J. Chem. Physik*, **22**, 51 (1817); *Ann. Chim. Phys.*, **17**, No. 2, 5 (1921); *Ann. Physik*, **4**, 153 (1825); *ibid.*, **6**, 331, 369 (1826); *ibid.*, **7**, 261 (1826).

since because of the large number of atoms which the empirical formulas indicate must be contained in the structure of their molecule-ions.

The heteropoly acids are usually described in terms of the number of molybdenum, tungsten, and/or vanadium atoms associated with the other anionic atom, such as phosphorus, in the simplest formula. In general, it appears that there are three main classes of heteropoly acids. These are the 6-poly-, the 9-poly-, and the 12-polyacids. In the well-characterized 6-polyacids, the "other" atom is usually I, Te, Fe, Cr, Al, Co, Rh, and Mn—all of which can exhibit six-fold coordination with oxygen in their anions. The 9-poly- and 12-polyacids, on the other hand, are usually based on P, As, Si, Ti, Ge, B, Sn, Zr, Th, and Ce, the first five of which customarily have four-fold coordination with oxygen in their anions.

The fact that 6-poly-, 9-poly-, and 12-polyacids are so extremely common prompted Miolati and Rosenheim[207] to suggest that the "other" atom is the central atom in a Werner-type complex involving peripheral molybdenum, tungsten, or vanadium oxides. Unfortunately, although their idea of a coordination complex in which the "other" atom has the central place was essentially correct, these authors and their many followers did not conceive of the anions of the heteropoly acids as truly three-dimensional structures and hence set up incorrect formulations. The first picture giving a reasonable approximation to the presently accepted structures of the heteropoly acids was given by Pauling.[208] Later work by Keggin[209] and other English crystal chemists has led to a reasonably sound structure for the heteropoly acids based on x-ray diffraction measurements. According to the x-ray data, the anions of the 9- and 12-polyacids consist of a central XO_4 tetrahedron sharing oxygen atoms with the proper number of surrounding MoO_6, WO_6, or VO_6 octahedra as shown in Figures 9-27 and 9-28. In the 6-polyacids, the central ion exhibits an octahedral coordination, XO_6, and this XO_6 group shares oxygen atoms with six MoO_6, WO_6, or VO_6 octahedra,[210] with all seven octahedra lying in the same plane to give a disk-shaped molecule-anion.

Heteropoly Acid Structures from X-Ray Diffraction

The first structure for a 12-polyacid was determined[209] on a cubic crystal

[207] A summary of this viewpoint is given by A. Rosenheim in *Abegg's Handbuch der anorganischen Chemie*, S. Hirzel, Leipzig, 1921, Vol. IV, Pt. I, ii, pp. 977–1065.

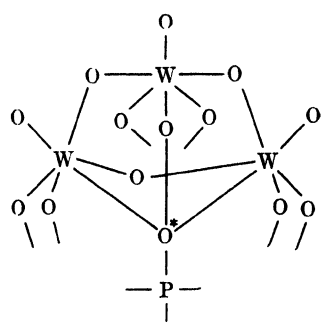
[208] L. Pauling, *J. Am. Chem. Soc.*, **51**, 2868 (1929).

[209] J. F. Keggin, *Proc. Roy. Soc. (London)*, **A144**, 75 (1934); *Nature*, **131**, 908 (1933); *ibid.*, **132**, 351 (1933).

[210] J. S. Anderson, *Nature*, **140**, 850 (1937); H. T. Evans, Jr., *J. Am. Chem. Soc.*, **70**, 129 (1948).

having the empirical formula $9\ H_2O \cdot P_2O_5 \cdot 24\ WO_3$. A drawing of the anion in this phosphododecatungstic acid is shown in Figure 9-27, in which it can be seen that the central PO_4 group is surrounded by 12 WO_6 octahedra arranged in groups of three. One oxygen in each of these WO_6 octahedra is connected to only one tungsten atom, whereas four others are shared between two tungsten atoms, thereby holding the outer shell of WO_6 octahedra together. The sixth oxygen in each WO_6 octahedron is shared between three tungsten atoms and the central phosphorus atom. This type of oxygen, of which there are four in the entire anion, serves to tie the structure together. It represents an unusual variety of oxygen atom in that it has a coordination number of four and hence probably exhibits sp^3-bonding.* The other oxygens in the structure are believed to show the usual p- or p^2-bonding.

According to the structure given for the anion in Figure 9-27, the formula of the acid studied must be $H_3[P(W_3O_{10})_4] \cdot 3\ H_2O$. Due to the way that the molecule-ion is tied together in three dimensions, it is practically impossible to write an intelligible two-dimensional structural formula for it. However, the chemical formula for one of the W_3O_{10} groups is shown below, as it is attached to the phosphorus atom and with four extra oxygen atoms borrowed from other W_3O_{10} groups with which these oxygens are shared. In this formula, the oxygen in sp^3-bonding is denoted with an asterisk.



(9-27)

The crystal structure[211] of another 12-polyacid having the empirical formula $61\ H_2O \cdot P_2O_5 \cdot 24\ WO_3$ was shown to be based on the same anion as given in Figure 9-27. This acid, therefore, has the formula $H_3[P(W_3O_{10})_4] \cdot 29\ H_2O$. In this structure determination, the positions of the 29

* The terms (such as sp^3, p^2, d^2sp^3) used here to describe various hybridizations are only approximations based on the atomic geometry. Obviously, a careful quantum-mechanical study would lead to somewhat different hybridizations.

[211] A. J. Bradley and J. W. Illingworth, *Proc. Roy. Soc.* (*London*), **A157**, 113 (1936).

molecules of water were also calculated, and the water molecules were found to be regularly placed between the large $(PW_{12}O_{40})^{3-}$ anions. This structure study is of particular interest, in that it shows how a number of small molecules (the water), and presumably how equivalently small ions, can be packed around the large $[P(W_3O_{10})_4]^{3-}$ anion.

Crystallographic and x-ray diffraction studies of a large number of 12-polyacids have indicated that the anions in each case have a structure identical to the one shown in Figure 9-27. Thus, the pentahydrates of sodium, potassium, rubidium, cesium, and thallium phosphododecatungstates or phosphododecamolybdates[212] have structures very similar to the phosphododecatungstic acid pentahydrate, described by Keggin.[209] All of these salts contain the anion depicted in Figure 9-27. The silver phosphododecatungstate either in anhydrous form or as the dihydrate has also been shown to contain this same anion.[213] It is also interesting to note that ethyl sulfoxide phosphododecatungstate is isomorphic[214] with the phos-

$$|(C_2H_5)_2\overset{O}{S}\rightarrow O\leftarrow\overset{O}{S}(C_2H_5)_2|_3\cdot|P(W_3O_{10})_4|(OH)_3$$

phododecatungstate 29-hydrate studied by Bradley and Illingworth.[211] This indicates that the crystal structure is primarily determined by the large phosphododecatungstate anion, and that even such a complicated counter ion as ethyl sulfoxide can be fitted between the large anions of the 12-polyacid.

Not only do the phosphododecatungstates and phosphododecamolybdates exhibit the anion shown in Figure 9-27, but this same anionic structure is generally found in the 12-polyacids based on elements other than phosphorus. This has been demonstrated[212,215] by crystallographic work on arsenotungstates, arsenomolybdates, silicotungstates, silicomolybdates, borotungstates, manganimolybdates, germanitungstates, and others. The extensive series[216] of isomorphous compounds and the formation of solid solutions between various compounds of the 12-polyacids indicate that the anion in all cases has the type of structure shown in Figure 9-27. It is also

[212] J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, **1935**, 575.

[213] J. R. de A. Santos, *Rev. fac. ciênc., Univ. Coimbra*, **16**, 5 (1947).

[214] F. P. Vaquer, *Mem. acad. ciênc., artes (Barcelona)*, **28**, 175 (1946); also see J. de P. de Teresa, *Anales fís. y quím. (Madrid)*, **40**, 385 (1944); *ibid.*, **42**, 495 (1946).

[215] J. A. Santos, *Proc. Roy. Soc. (London)*, **A150**, 309 (1935).

[216] For example, J. L. Hoard, *Z. Krist.*, **84**, 217 (1933); O. Kraus, *ibid.*, **100**, 394 (1939); *Naturwiss.*, **25**, 250 (1937); A. Ferrari and O. Nanni, *Gazz. chim. ital.*, **69**, 301 (1939); A. Ferrari, L. Cavalca, and M. Nardelli, *ibid.*, **78**, 551 (1948); A. Ferrari L. Cavalca, M. Nardelli, A. Selegari, and M. Cingi, *ibid.*, **79**, 61 (1949).

interesting to note that water can often be removed from highly hydrated 12-polyacids and their salts without affecting the x-ray pattern; and, conversely in some cases, water can be taken up by the crystal without changing its structure. Again, it appears that the crystal structure is primarily determined by the large, roughly spherical anions, and that the other constituents are fitted between these anions to give a structure that is at least superficially similar to that of the zeolites.

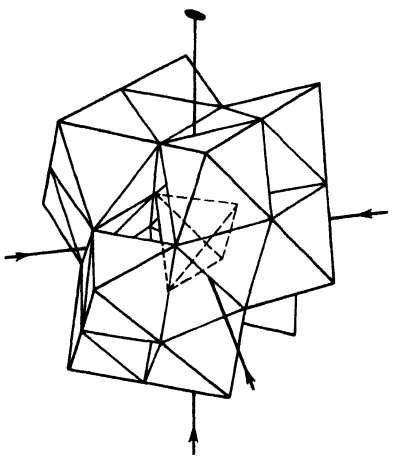


Fig 9-27. Structure of the $(PW_{12}O_{40})^{3}$ anion in the 12-polyacids. The PO_4 tetrahedron is shown with dotted lines, whereas the WO_6 or MoO_6 octahedra are drawn with solid lines.

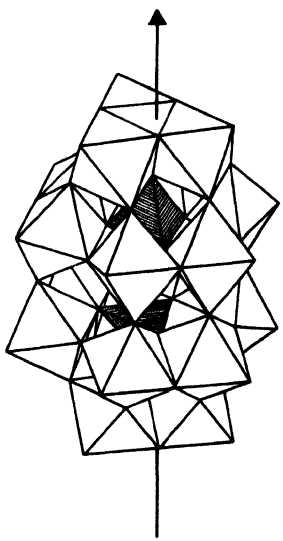
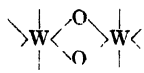


Fig. 9-28. Structure of the $(P_2W_{18}O_{62})^{6}$ anion in the 9-polyacids. The PO_4 tetrahedra are shaded in this diagram, whereas the WO_6 or MoO_6 octahedra are not.

The structure of the 9-polyacid was determined by Dawson[217] on a potassium phosphononatungstate having the following empirical formula: $3\ K_2O \cdot 14\ H_2O \cdot P_2O_5 \cdot 18\ WO_3$. The structure of the anion found in this salt is shown in Figure 9-28, where it can be seen that two PO_4 tetrahedra are involved with 18 WO_6 octahedra. At the top and bottom of the structure, as oriented in Figure 9-28, there are W_3O_{10} groups similar to the four W_3O_{10} groups making up the tungsten-oxygen cage of the anion of the 12-

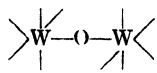
[217] B. Dawson, *Acta Cryst.*, **6**, 113 (1953).

polyacid shown in Figure 9-27. In addition, there are six pairs of WO_6 octahedra which share two oxygen atoms between them so as to form a



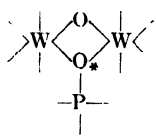
(9-28A)

linkage. Each of these WO_6 octahedra has one oxygen atom in an isolated position and three other oxygens which are shared between two tungsten atoms so as to form a



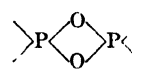
(9-28B)

inkage. One of the two oxygen atoms shared within the pair of WO_6 octahedra is also shared with the PO_4 tetrahedra. This oxygen thus probably exhibits sp^2-bonding as shown by the following atomic arrangement in which the oxygen in question is marked by an asterisk



(9-28C)

It should be noted that four-membered rings, such as the one shown above, formula 9-28A, involving tungsten and oxygen atoms, have not been found in the condensed phosphates (see Chapt. 8), and such postulated dimetaphosphate



linkages [redacted] molecular structures have been predicted[218] to be points of strain. Presumably, this difference between tungstates and phosphates is due to the fact that the tetrahedral angle in the sp^3-bonding of the phosphorus leads to the unacceptably small maximum angle of 76° between the two bonds from the oxygen, whereas the octahedral angle in the d^2sp^3-bonding of the tungsten allows 90° for the angle between the two bonds from the oxygen—a value which is normal for pure p^2-hybridization.

As can be seen from Figure 9-28, the pairs of WO_6 octahedra are arranged in two rings, each built up of three pairs of octahedra. In this structure, there are two oxygen atoms exhibiting sp^3-bonding, six oxygens exhibiting sp^2-bonding, 18 oxygens exhibiting p-bonding, with the remainder holding tungsten atoms together by p^2-bonds. Although these anionic structures have been discussed in terms of covalent bonds, it is possible that the

W—O—W and Mo—O—Mo bonds are primarily ionic. More work of a detailed nature is needed to elucidate this question.

In addition to the crystal-structure examinations reported above, some x-ray diffraction studies have been carried out on solutions of phosphomolybdates and phosphotungstates.[219] These investigations have given results in accord with existing theories of the structure of liquids.

Chemical and Physical Properties of the Heteropoly Acids

The formation of the heteropoly acids and salts depends on the concentration of the reacting substances, the temperature, and the acidity. The reacting substances to make a phosphorus-based heterpoly acid are any orthophosphate or material hydrolyzing to give an orthophosphate in acidic solution and the oxides, acids, or salts of tungsten, molybdenum, and vanadium. The concentrations affect the results according to the law of mass action. The phosphododecamolybdic and phosphododecatungstic acids are readily formed at room temperature, but the equivalent 9-polyacids usually require boiling. The most important factor in the formation of heteropoly acids is the acidity. Phosphoric acid and sodium molybdate when mixed in any proportion will not form a complex acid, whereas addition of hydrochloric acid equivalent to the amount of sodium molybdate leads to the formation of a mixture of the 9- and 12-polyacids, with the yield of the latter increasing with acidity. Methods of making the heteropoly acids and salts containing phosphorus have been given in considerable detail in the literature.[220,221] It should be noted that the use of ion exchange resins appears to be a valuable new tool for the study and preparation of heteropoloy acids.[222]

At least in the 12-polyacids, phosphorus, tungsten, vanadium, and molybdenum can substitute for each other in a given crystal.[223] It is also

[219] G. Porod, *Kolloid-Z.*, **125**, 51, 108 (1952); J. A. Prins and R. Fonteyne, *Physica*, **2**, 1016 (1935).

[220] For example, J. C. Bailar, Jr., *Inorganic Syntheses*, **1**, 132 (1939); H. Wu, *J. Biol. Chem.*, **43**, 189 (1920); T. J. Hastings and H. A. Frediani, *Anal. Chem.*, **20**, 382 (1948).

[221] For a review of the early literature on phosphomolybdates, phosphotungstates, and phosphovanadates, see J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1931, Vol. IX, pp. 826–36 (vanadium); Vol. XI, pp. 659–72 (molybdenum); Vol. XI, pp. 862–74 (tungsten). For a recent brief review of heteropoly and isopoly acid, see L. F. Audrieth and R. K. Osterheld, *Encyclopedia of Chemical Technology*, eds. R. E. Kirk and D. F. Othmer, Interscience Publishers, Inc., 1954, Vol. 7, pp 458–65; also *Bulletin Cdb-12* of the Climax Molybdenum Co., New York, October, 1956.

[222] L. C. W. Baker, B. Loev, and T. McCutcheon, *J. Am. Chem. Soc.*, **72**, 2374 (1950).

[223] W. Blum, *J. Am. Chem. Soc.*, **30**, 1858 (1909); G. Canneri, *Gazz. chim. ital.*, **56**, 642 (1926); *ibid.*, **56**, 871 (1926); F. Rodolico, *Atti accad. Lincei*, **4**, No. 6, 471 (1926).

interesting to note that in the 12-polyacids more cations, such as sodium, than correspond to the three replaceable hydrogens of the acid can be incorporated into the crystal structure.[221,224] Presumably, these ions fit into the spaces between the large heteropoly anions in the crystal lattice and their charges are counterbalanced by other small ions of opposite charge, *e.g.*, OH^-. Anions appear to fit into the crystal in the same way, so that "nitrophosphomolybdates" are known.[225] A number of phosphomolybdates and phosphotungstates have been prepared containing metal amines as cations.[226] Thus, for example, the 12-poly salts of the cations consisting of copper coordinated with 8-pyridine molecules and nickel coordinated with 2-ethylene diamine molecules have been made. Organic bases such as the amines and the alkaloids have also been combined with either phosphotungstates or phosphomolybdates to give crystalline salts.[227] In these compounds and in the salts containing metal ions, the number of cations which are to be found appears to depend on the packing of the cations in the crystal, rather than the charge on the heteropoly anion.

The 12-polyacids, as well as several of the other heteropoly acids, are usually very soluble in solvents containing oxygen in the molecule[228]—*i.e.*, in water, ether, alcohols, esters, ketones, and aldehydes—but are less soluble in such solvents as benzene, which contain no combined oxygen. The heterpoly acids can be extracted from aqueous solution by ether to form a system of three layers, with ether at the top, an aqueous layer next, and at the bottom a saturated solution of the heteropoly acid in ether. This property of dissolving in organic solvents is often used in the preparation and purification of the heteropoly acids

[224] E. A. Nikitina, *J. Gen. Chem. (U.S.S.R.)*, **14**, 769 (1944), *ibid.*, **10**, 779, 997 (1940), *Compt. rend. acad. sci. U.R.S.S.*, **26**, 370 (1940); G. B. Bokii, *Trudy Inst. Krist. Akad. Nauk S.S.S.R.*, **1947**, No. 3, 19.

[225] T. Gaspar y Arnal, *Ann. chim. anal. et chim. appl.*, **11**, 97 (1929); *Anales soc. espan. fis. y quim.*, **26**, 435 (1928). A similar case may be found in the aluminophosphotungstates such as are described by L. C. Daniels, *J. Am. Chem. Soc.*, **30**, 1846 (1909).

[226] M. Jean, *Compt. rend.*, **223**, 155 (1946), H. A. Horan, *J. Am. Chem. Soc.*, **61**, 2022 (1939), G. Spacu and V. Nicolaescu, *Bull. sect. sci. acad. roumaine*, **22**, 130 (1939); *Bul. Soc. Stiinte Cluj*, **9**, 347 (1939).

[227] M. E. Kahane and E. Kahane, *Bull. soc. chim. France*, **1952**, 1068; L. Lematte, G. Boinot, E. Kahane, and M. E. Kahane, *Compt. rend.*, **191**, 1130 (1930); G. Spacu and V. Nicolaescu, *Bull. sect. sci. acad. roumaine*, **22**, 337 (1940); A. Tettamanzi, *Atti accad. sci. Torino, Classe sci. fis., mat. nat.*, **71**, 116 (1936); J. Krepelka and O. Stieber, *Collection Czech Chem. Communs.*, **11**, 540 (1939); N. V. Maksimova and M. T. Kozlovskii, *Zhur. Anal. Khim.*, **2**, 353 (1947).

[228] A. G. Schroggie, *J. Am. Chem. Soc.*, **51**, 1057 (1929); C. Wadelin and M. G. Mellon, *Anal. Chem.*, **25**, 1668 (1953).

Because the anions have an extremely high molecular weight, the heteropoly acids and their salts act as good precipitating agents for cations of high molecular weight. As indicated in the preceding paragraph, where the alkaloid salts of the heteropoly acids were mentioned, some of these precipitates are crystalline. However, amorphous precipitates have also been produced. At pH values below the isoelectric point of proteins (at which pH the heteropoly anions are stable and do not dissociate), heteropoly anions will precipitate proteins[229] -which are, of course, cationic under these conditions. At various times this has formed the basis of procedures for separating and analyzing proteins. The same phenomenon of precipitation of high molecular weight cations by high molecular weight anions is found in the interaction of heteropoly acids with basic dyes. The precipitates formed by interacting[230] such basic dyes as Rhodamine B with phosphotungstic or phosphomolybdic acids are used as toners in printing. The resulting lakes exhibit excellent permanency to light but are somewhat alkali sensitive.

The heteropoly acids also act as ion exchange solids. This phenomenon has been treated theoretically.[231] Related to this is the ability of the heteropoly acids to absorb gases and vapors apparently by entrapping them in their large crystal lattice. In a study of absorption of a number of vapors by ammonium phosphododecamolybdate, it was found that the phosphomolybdate changed in color from yellow to a more or less deep green when organic vapors were adsorbed.[232] Presumably, the color change indicates reduction of the molybdenum and oxidation of the adsorbate, but no change in weight was observed, and the adsorption appeared to be reversible.

Some examination has been made of the solubility of phosphorus-based heteropoly compounds,[233] and a phase diagram is available. In addition, a number of colorimetric studies have been carried out on solutions of the phosphotungstates and phosphomolybdates;[234] and the constitution of

[229] P. Cristol, J. Fourcade, and C. Benezech, *Trav. membres soc. chim. biol.*, **23**, 1107 (1941); D. Mitchell, E. H. Shaw, Jr., and G. G. Frary, *Proc. S. Dakota Acad. Sci.*, **24**, 108 (1944).

[230] A. Linz and L. W. Coffer, *Am. Ink Maker*, **17**, No. 9, 39, 55, 57, 59, 61, 63, 65, 67, No. 10, 29, 31, 33, 35, No. 11, 27, 29, 31, 33, 45 (1939).

[231] D. Meier and W. D. Treadwell, *Helv. Chim. Acta*, **34**, 155 (1951).

[232] C. Tourneux and C. Devin, *Compt. rend.*, **232**, 2430 (1951); *ibid.*, **233**, 43 (1951).

[233] P. Souchay, *J. chim. phys.*, **42**, 61 (1945); A. V. Rakovskii and E. A. Nikitina, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 50 (1936).

[234] For example, M. Milletti and M. Giannini, *Chimica* (*Milan*), **6**, 192 (1951); P. Krumholz, *Z. anorg. u. allgem. Chem.*, **212**, 91 (1933); D. F. Boltz, T. de Vries, and M. G. Mellon, *Anal. Chem.*, **21**, 563 (1949).

solutions of heteropoly acids has been investigated in considerable detail by a number of different techniques,[235] including cryoscopy, pH titration, potentiometric measurements, and diffusion studies. At the present time, about the only general statement that can be made is that the solutions at very low pH values probably contain approximately the same anions as are found in the crystals, but as the pH is increased these anions appear to break up into fragments similar, if not identical, to the polymolybdates at the same pH.[236]

A number of reducing agents such as stannous chloride, ascorbic acid, and metallic molybdenum reduce the phosphomolybdates and phosphotungstates to blue compounds.[237] Colorimetric studies of the reduced forms of molybdenum and tungsten heteropoly acids of phosphorus, arsenic, boron, and silicon indicate that the blue color is attributable to the molybdenum and tungsten, and that the central atoms in the anion play a secondary role.[238] It is believed that change of the yellow heteropoly acid to the blue form is due to reduction of only a few of the peripheral molybdenum or tungsten atoms in the heteropoly anion. Some of these blue, reduced forms of the heteropoly acids have been crystallized, and in these crystals the MoO_3/MoO_2 ratio is found to range around 4–5. Blue compounds which are believed to be similar to the ones obtained by reduction can be prepared by merely heating the yellow phosphomolybdic acid to remove sufficient water so as to cause breakdown of the crystal structure.[239] In this case, the blue material is amorphous. There is also some literature on the preparation of perphosphomolybdic and perphosphotungstic acids.[240]

The Mo/P and the W/P mole ratios in the phosphomolybdic and phosphotungstic acids which have been described in the early literature[221] range from 2 to about 25. Presumably, some of these reported compounds are

[235] For example, P. Souchay and J. Faucherre, *Bull. soc. chim. France*, **1951**, 355; O. Lamm, *Svensk. Kem. Tidskr.*, **56**, 37 (1944); G. Jander and E. Drews, *Z. physik. Chem.*, **A187**, 149 (1940); *ibid.*, **A190**, 195, 217 (1942); G. Jander and K. F. Jahr, *Kolloid-Beih.*, **41**, 297 (1934).

[236] I. Lindquist, *Nova Acta Regiae Soc. Sci. Upsaliensis*, **15**, No. 1, 1 (1950).

[237] C. Ferrari, *Gazz. chim. ital.*, **81**, 795 (1951); V. Auger and N. Ivanoff, *Compt. rend.*, **204**, 1424 (1937); A. Verda, *Pharm. Acta Helv.*, **3**, 4 (1928); G. Denigès, *Bull. soc. pharm. Bordeaux*, **65**, 107 (1927); *Compt. rend.*, **185**, 687 (1927); M. Rindl, *S. African J. Sci.*, **11**, 362 (1916); also see ref. 220.

[238] Z. M. Vaĭsberg and B. Ya. Daĭn, *Zhur. Obshcheĭ Khim.*, **18**, 1037 (1948).

[239] M. Nardelli and O. Scaglioni, *Gazz. chim. ital.*, **81**, 464 (1951).

[240] V. Macri, *Bull. chim. farm.*, **56**, 417 (1917); E. P. Alvarez, *Chem. News*, **94**, 269 (1907).

amorphous materials or mixtures of different crystals. It is also quite conceivable that simple phosphate, molybdate, or tungstate ions can be incorporated into the complicated crystals of the 9-polyacids and the 12-polyacids. Since the 9-polyacids and 12-polyacids based on phosphorus have been emphasized in the literature of the last few decades, it would seem that the two structures shown in Figures 9-27 and 9-28 are a key to the entire problem of the heteropoly acids of phosphorus. However, it is quite possible that other complicated anions will be proved to exist through additional studies. However, it is very difficult to believe that phosphorus can assume the sp^3d^2-hybridization required by the central atom in the known 6-polyanion.[210] Although phosphorus exhibits sp^3d^2-bonding in such compounds as the pentahalides, this hybridization should not be expected in the presence of appreciable amounts of water.

The phosphovanadates have not been studied nearly so extensively as the phosphomolybdates. As previously pointed out,[223] phosphododecavanadates are well known.[241] In addition, the early literature[221] indicates a large number of compounds in which the V/P mole ratio is 1 or 2. An early classification of the heteropoly acids involving vanadium and phosphorus was into the luteophosphovanadates and the purpureophosphovanadates, where "luteo" referred to the yellow-colored compounds, and the "purpureo" referred to deep red or purple-colored compounds. Phosphododecavanadic acid and its salts belong to the class of purpureo compounds, whereas the compositions in which the V/P ratio is small (1 or 2) are luteophosphovanadates. Although the existence of heteropoly acids of chromium has not been well established, it appears that there are some compounds in the anions of which there are several moles of chromium to one of phosphorus.[242]

It should be noted that hypophosphites, phosphites, and pyrophosphites apparently can be incorporated into heteropoly acids as well as orthophosphates.[243] Similar behavior is also found in the case of arsenic, since arsenites as well as arsenates can be incorporated into heteropoly acids.

[241] A. Rosenheim and M. Pieck, *Z. anorg. u. allgem. Chem.*, **98**, 223 (1916); P. Souchay and S. Dubois, *Ann. chim.*, **3**, No. 12, 88 (1948).

[242] I. Mozkin, *Ueber Kondensationsproducte von Phosphaten, Arsenaten oder Nitraten der Alkalien mit Chromaten oder Sulfaten derselben*, Berlin, 1894; C. Friedheim and I. Mozkin, *Z. anorg. Chem.*, **6**, 284 (1894); M. Blondel, *Compt. rend.*, **118**, 194 (1894).

[243] F. Mawrow and N. Nikolow, *Z. anorg. u. allgem. Chem.*, **93**, 170 (1915); A. Rosenheim, A. Wolff, J. E. Koch, and N. Siao, *ibid.*, **193**, 47 (1930); A. Rosenheim and A. Wolff, *ibid.*, **193**, 64 (1930); A. Rosenheim, W. Weinberg, and J. Pinsker, *ibid.*, **84**, 217 (1914); A. Rosenheim, M. Schapiro, and A. Italiener, *ibid.*, **129**, 196 (1923).

ORGANIC ORTHOPHOSPHATES

Preparation of Organic Orthophosphates

A very large number of organic orthophosphates have been described in the literature.[244] These include the esters of orthophosphoric acid: alkyl orthophosphates, aryl orthophosphates, and esters in which the organic radicals have functional groups on them. Common examples of the latter class are the sugar phosphates and the glycerophosphates. In addition, there are the mixed anhydrides of organic acids and orthophosphoric acid, an example of which is acetyl phosphate.

Quite a number of different methods have been used to make phosphate esters.[244] Commercial preparation of phosphate esters is commonly carried out by slowly adding phosphorus oxychloride to the appropriate alcohol or phenol in a well-stirred, closed vessel. Generally, the alcohols are more reactive than phenols, and thus the alcohol reaction can be carried out at a lower temperature. Esters such as triphenyl phosphate are made by adding phosphorus oxychloride to sodium phenolate dissolved in a hydrocarbon or by simply refluxing the phenol with phosphorus oxychloride. In the preparation of mixed esters, the alcohol or the phenol is added to the phosphorus oxychloride, so that the first equivalent of alcohol will form a dichlorophosphate, the chlorine atoms of which can then be replaced by other alcohols. To avoid undesirable substitution, mixed esters are usually made at low temperatures, and a scavenger, such as pyridine or other alkali, is employed to remove the liberated hydrogen chloride and carry the reaction to completion. Orthophosphate esters can also be prepared by reacting phosphorus pentoxide with alcohols or phenols.[244,245] Direct esterification of alcohols by phosphoric acid can be carried out, but it is usually necessary to use high temperatures and reduced pressures. Acid salts of orthophosphoric acid will also form esters in the presence of alcohols at elevated temperatures For example, glycerol and monosodium phosphate yield a mixture of monoglycero- and diglycerophosphates upon heating for several hours at 175°C. under reduced pressure. Preparation of various orthophosphate esters is reviewed by Kosolapoff.[241]

One of the best ways of making mixed anhydrides of organic acids and orthophosphoric acid is by reacting the chloride of the organic acid with a salt of the phosphate. Commonly, the silver salt is used. Thus, trisilver

[244] For a brief review of the subject, see G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950, Chapt. 9, pp. 220–77. For fluorocarbon derivatives, see K. Sellars, *J. Applied Chem.*, **6**, 45 (1956).

[245] E. Cherbuliez and H. Wenger, *Helv. Chim. Acta*, **28**, 1584 (1945).

phosphate reacts with an excess of acetyl chloride in cold ether to form triacetyl phosphate.[241] Silver phosphates have also been used in synthesizing a number of different esters, as well as in making condensed phosphates themselves.[244] Phosphoric acid can, under some conditions, be directly acylated. For example, monoacetyl phosphoric acid can be prepared by passing ketene, $H_2C{=}C{=}O$, with good cooling into 85% phosphoric acid in ether and hydrolyzing the resulting mixture with ice water.[246] The acetyl phosphate can be separated from the excess inorganic phosphate by addition of barium hydroxide, since the simple barium phosphate is quite insoluble, and barium acetyl phosphate is soluble in water. Another interesting reaction for the synthesis of acetyl phosphate is based on isopropenyl acetate.[247] This reaction, which has been carried out in *n*-butyl ether with a trace of sulfuric acid as catalyst, is described by the following equation:

$$H_2C{=}C(CH_3)OCCH_3 + (HO)_3PO \longrightarrow CH_3COP(O)(OH)_2 + CH_3CCH_3 \quad (9\text{-}29)$$

This reaction goes to the right because transfer of the acetyl group from the isopropenyl radical allows this radical to convert from the enol to the considerably more stable keto form (the acetone of equation 9-29).

In all of the organic orthophosphates discussed so far, the carbon and phosphorus atoms are linked together through an oxygen atom. However, the literature contains descriptions of a few compounds which can truly be classed as organic orthophosphates, but which have elements in addition to oxygen between the phosphorus and the carbon atoms. An example of this type of compound is found in the tris(trialkylsilyl) phosphates[248] which have the formula $(R_3SiO)_3PO$.

Organic Orthophosphates of Biological Interest

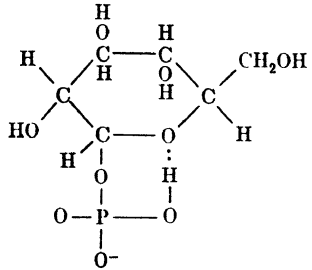
In modern biology, it is becoming daily more evident that phosphorus compounds play a major role in life processes. Many of the biologically important phosphorus compounds are orthophosphates. Although it would take an entire book to do justice to the chemistry of the biologically important orthophosphates, an attempt will be made here to review briefly some of the major classes of compounds in this category.

[246] R. Bentley, *J. Am. Chem. Soc.*, **70**, 2183 (1948); C. D. Hurd and M. F. Dull, *ibid.*, **54**, 3427 (1932).

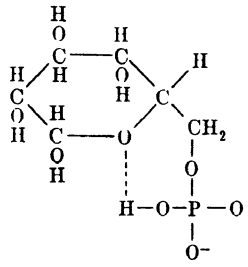
[247] D. E. Koshland, Jr., *J. Am. Chem. Soc.*, **73**, 4103 (1951).

[248] M. G. Vorankov, *J. Gen. Chem. (U.S.S.R.)*, **25**, 469 (1955).

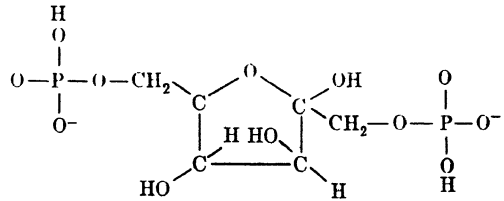
TABLE 9-7
Sugar Phosphates, Nucleic Acid, and Nucleotides



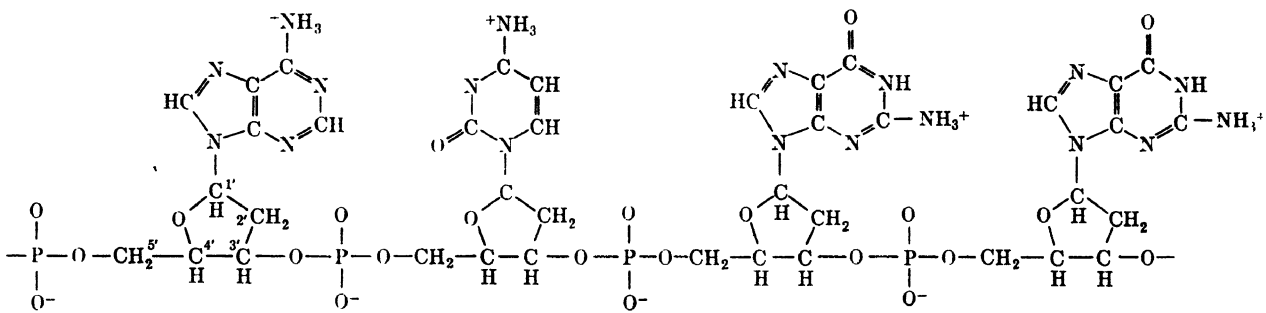
Glucose-1-phosphoric acid



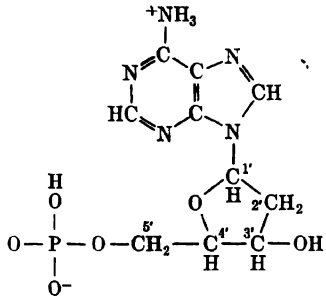
Glucose-6-phosphoric acid



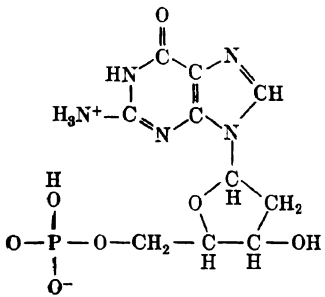
Fructose-1,6-diphosphoric acid



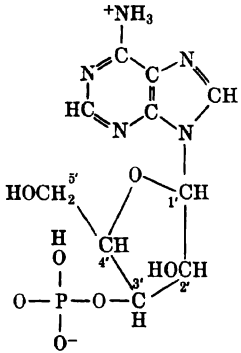
Fragment of a chain of desoxyribonucleic acid



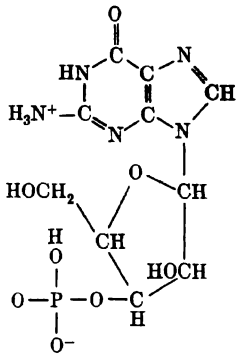
Desoxyadenylic acid



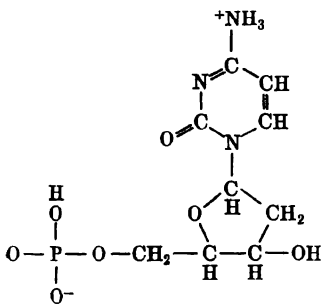
Desoxyguanylic acid



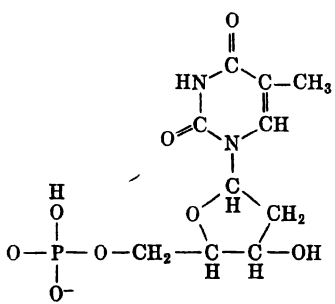
Adenylic acid



Guanylic acid

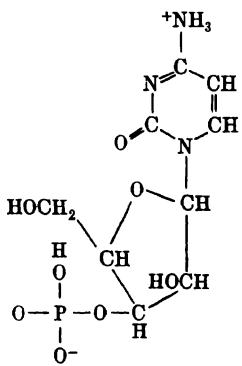


Desoxycytidylic acid

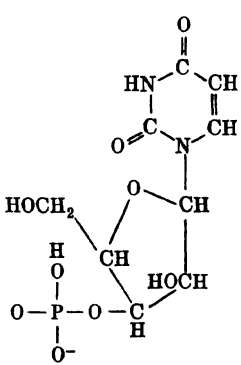


Thymidylic acid

Nucleotdes from desoxyribonucleic acid



Cytidylic acid



Uridylic acid

3'-Phosphate nucleotides from ribonucleic acid

The sugar phosphates play an important role in photosynthesis[249] and metabolism.[250] The structures of three sugar phosphates are shown in Table 9-7. These structural formulas depict the sugar phosphates with the type of hydrogen bonding that is to be expected in acid solution. A number of sugar phosphates involving different sugars have been found in living systems, and there are quite a few examples of sugars in which several OH groups have been esterified by phosphoric acid The alternate case where two sugar molecules are attached to a given PO_4 group is also known in biology, and extremely long chains of alternating PO_4 groups and sugar moieties are found in the nucleic acids.

Two types of nucleic acids are known.[251] These are the desoxyribonucleic acids and the ribonucleic acids, which do not occur in free form in the cells but are combined with proteins in complicated structures called nucleoproteins.[252] In all cells possessing nuclei, desoxyribonucleic acids, which were originally called thymonucleic acids, are believed to exist solely in the nucleus and are primary components of chromosomes This type of nucleic acid is also found in noncellular parasites[253] such as bacteriophages, certain animal viruses, and rickettsia. The ribonucleic acids, originally called yeast nucleic acids, occur in both the nucleus and cytoplasm of living cells. So far, only the ribonucleic acids have been isolated from plant viruses, and only deoxyribonucleic acids from bacteriophages. Animal viruses may contain both types of nucleic acids, but this is not clearly known because of contamination with nucleic acids from the cells of the host.[253] Desoxyribonucleic acids and ribonucleic acids are large molecules having molecular weights varying from several thousand to a few million, as they have been studied. Commercial preparations of these chemicals have undergone considerable depolymerization in purification, so that they no longer exhibit the biochemical activity of the native substances.

[249] E. Rabinowitch, *Photosynthesis and Related Processes*, Interscience Publishers, New York, Vol. 1, 1945; Vol. 2, 1951; A. H. Brown and A. W. Frenkel, *Ann. Rev. Plant Physiol.*, **4**, 23 (1953); W. Vishniac, *ibid.*, **6**, 115 (1955); D I. Arnon, *ibid.*, **7**, 325 (1956).

[250] W. D. McElroy and B. Glass, *Phosphorus Metabolism*, Johns Hopkins Press, Baltimore, 1952, Vols. I and II; H. Albaum, *Ann. Rev. Plant Physiol.*, **3**, 35 (1952).

[251] J. N. Davidson, *The Biochemistry of the Nucleic Acids*, John Wiley & Sons, Inc., New York, 1950; L. Laufer and D. R. Schwarz, *Encyclopedia of Chemical Technology*, ed. R. E. Kirk and D. F. Othmer, Interscience Publishers, 1952, Vol. 9, pp. 508–15; "Nucleic Acid," *Symposia Soc. Exptl. Biol.*, **1947**, No. 1.

[252] F. H. C. Crick, *Proc. Natl. Acad. Sci.*, **40**, 756 (1954); *Sci. American*, **191**, No. 4, 54 (1954); M. H. F. Wilkins *et al.*, *Nature*, **172**, 759 (1953)

[253] R. Markham, *Advances in Virus Research*, Academic Press, New York, 1953, Vol. I, pp. 315–30; C. A. Knight, *ibid*, 1954, Vol. II, pp. 165–74.

In the desoxyribonucleic acids there are four kinds of bases, one kind of pentose sugar (2-desoxyribose), and orthophosphate groups. The four bases consist of two pyrimidines (cytosine and thymine) and two purines (adenine and guanine). Desoxyribonucleic acids have been shown to have a chain structure consisting of alternate sugar moieties and PO_4 groups.[254] The bases are attached to a carbon of the sugar by an N—C bond. A segment of a desoxyribonucleic acid chain is shown in Table 9-7 in which the recurring 3′:5′ phosphodiester linkage is employed.[254]

Ribonucleic acids contain nearly the same chemical units as desoxyribonucleic acids, with the exceptions that (1) uracil replaces thymine as a base and (2) ribose (an OH in position 2′) takes the place of desoxyribose in the sugar part of the structure. Todd[254] and coworkers postulate a recurring 3′:5′ phosphodiester linkage in this type of structure, partially in analogy with the desoxyribonucleic acids, although it is recognized that branched structures are possible for the ribonucleic acids. In such a case, a 2′:3′ phosphodiester linkage would tie the branch to the main chain.

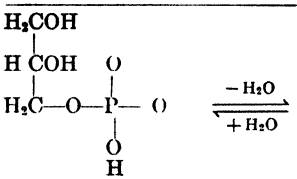
When the nucleic acids have been hydrolyzed to give a single sugar-phosphate moiety with the attached pyrimidine or purine base, the resulting compounds are called nucleotides. The structures of eight nucleotides (four from the ribonucleic acids and four from the desoxyribonucleic acids) are shown in Table 9-8. In reality, there are 12 nucleotides, with eight of them coming from the ribonucleic acids. That is, in addition to the set of four (shown in Table 9-8) in which the PO_4 group is attached at the 3′ position of the sugar, there are four similar nucleotides, derived from the ribonucleic acids, in which the PO_4 group is attached at the 2′ position. The double set of nucleotides from the ribonucleic acids is attributed to the formation of a cyclic intermediate during degradation of the ribonucleic acids.[254] Such a cyclic intermediate, an example of which is shown in Table 9-8 for the α- to β-glycerophosphoric acid interconversion, generally shows up in hydrolysis of phosphate esters in which there is a *cis*-hydroxyl group on the carbon atom adjacent to the point of attachment of the PO_4 group. The sugar moiety of the ribonucleic acids has such a hydroxyl group which is not present in the desoxyribonucleic acids. The cyclic intermediate which occurs in the hydrolysis of the ribonucleic acids favors the splitting of C—O—P linkages so that the ribonucleic acids are readily hydrolyzed in alkaline solutions to the nucleotide stage. On the other hand, the desoxyribonucleic acids resist hydrolysis, so that even hot alkalies do not depolymerize the structure as far as to the nucleotides. Thus, the

[254] See A. R. Todd, *Proc. Natl. Acad. Sci.*, **40**, 748 (1954) for a condensed review

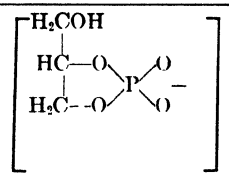
preparation of the four nucleotides of desoxyribonucleic acids shown in Table 9-7 involves enzymatic hydrolysis.

Another important class of phosphorus compounds in biology is the phospholipids[255] or phosphatides There are several classes of phospholipids

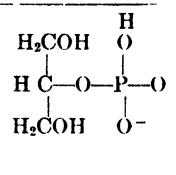
TABLE 9-8
Glycerophosphates and Some Phospholipids



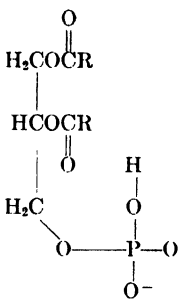
α-glycerophosphoric acid (two optically active forms)



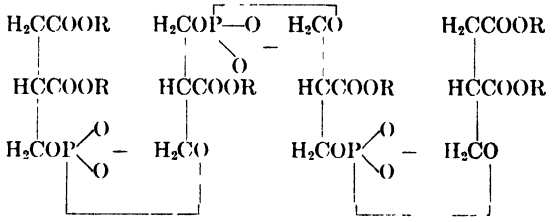
intermediate form



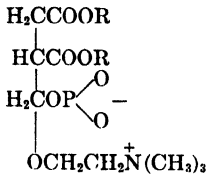
β-glycerophosphoric acid



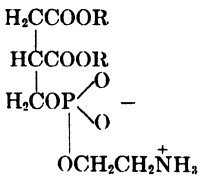
phosphatidic acid (where RCOOH = palmitic, oleic, and other fatty acids)



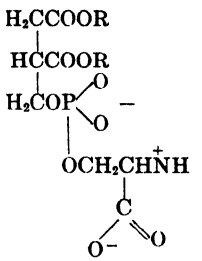
cardiolipin



phosphatidyl choline (lecithin constituent)



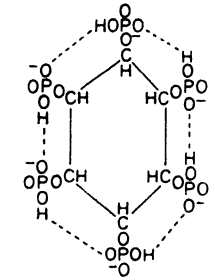
phosphatidyl ethanolamine (cephalin constituent)



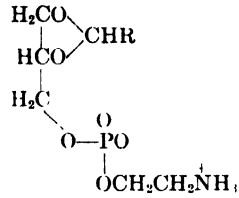
phosphatidyl serine (cephalin constituent)

[255] H. Wittcoff, *The Phosphatides*, Reinhold Publishing Corp., New York, 1951; J. A. Lovern, *The Chemistry of Lipids of Biochemical Significance*, Methuen and Co., London, 1955, pp. 6–24, 48–49, 94–95, 100–13, 122–24; H. J. Deuel, *Encyclopedia of Chemical Technology*, eds. R. E. Kirk and D. F. Othmer, Interscience Publishers, New York, 1952, Vol. 8, pp. 410–18; J. Stanley, *ibid.*, pp. 309–26.

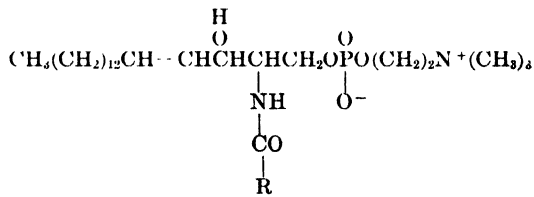
TABLE 9-8 (*continued*)



inositol hexaphosphate



a plasmalogen



sphingomyelin

One of them is the glycerophosphatides, which are derivatives of the glycerophosphoric acids. As shown in Table 9-8 there are two glycerophosphoric acids.[256] The α-form is optically active because four different groups are attached to the middle carbon atom. Conversion of the α- to the β-form often occurs in chemical reactions such as hydrolytic cleavage of the C—O- P linkage. It is believed that this takes place through a cyclic intermediate,[257] which is shown in Table 9-8. Because of this migration of the phosphorus, it is difficult to prove whether or not the β-form of glycerophosphoric acid occurs in the natural glycerophosphatides. Since optically active α-glycerophosphoric acid is obtained by enzymatic hydrolysis of phospholipids, it is certain that α-glycerophosphatide occurs in nature. If the α-glycerophosphate were produced from the β-form during hydrolysis of the glycerophosphatide, it would necessarily be the racemic mixture.

A number of salts of the glycerophosphates (usually a mixture of the β- and racemic α-forms) are known. As might be expected, the alkali metal salts are extremely soluble in water. Some of the other salts, such as ferric glycerophosphate (solubility = 50 g./100 ml. H_2O), have a surprisingly

[256] M. L. Moore, *Encyclopedia of Chemical Technology*, ed. R. E. Kirk and D. F. Othmer, Interscience Publishers, New York, 1951, Vol. 7, pp. 229–31.

[257] E. Chargaff, *J. Biol. Chem.*, **144**, 455 (1942); P. E. Verkade, J. C. Stoppelenburg, and W. D. Cohen, *Rec. trav. chim.*, **59**, 886 (1940); O. Bailly and J. Gaumé, *J. pharm. chim.*, **22**, 23 (1935); *Bull. soc chim.*, **2**, No. 5, 354 (1935).

high aqueous solubility. All of the glycerophosphates are quite insoluble in alcohol. Absolute glycerophosphoric acid is a colorless, odorless, syrupy liquid which is soluble in both water and alcohol. The acid tends to decompose during concentration, and hence it is usually sold as a 25–50% solution.

The simplest class of phospholipids, and the one most similar to the usual fat (the triglycerides), is derived from glycerophosphoric acid by esterification of the remaining two hydroxyl groups of the glycerol with fatty acids. Since phosphoric acid is tribasic and there remain two acidic hydrogens (one of them very weak), the final product is acidic and is known as a phosphatidic acid. When isolated from tissues, the phosphatidic acids are usually in the form of calcium or magnesium salts. A most interesting phosphatidic acid is the substance known as cardeolipin, which is believed to be a chain of three phosphatidic acids plus a diglyceride radical linked together through the PO_4 groups.[258] A condensed formula for cardeolipin is given in Table 9-8.

There are three closely similar phospholipids which are esters of phosphatidic acid and nitrogen-containing alcohols. These are the phosphatidyl esters of choline, ethanolamine, and serine, in which only one of the two available hydrogens on the PO_4 group of the phosphatidic acid is esterified. The choline derivative is an important constituent of lecithin, and the ethanolamine derivative is a major constituent of cephalin.

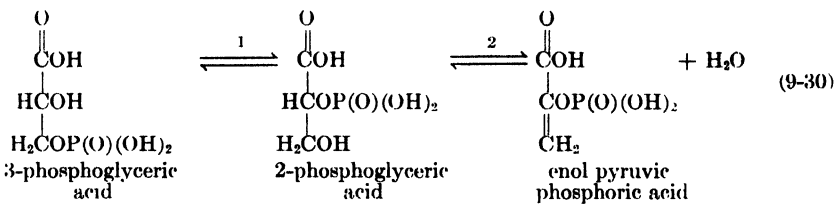
The inositol phosphatides or phosphoinositides are related to the phosphatidyl esters, in that one of the PO_4 groups of an inositol phosphate is esterified with the —OH group of a diglyceride. The structure of one of the inositols, inositol hexaphosphate (also called phytic acid or phytin) is shown in Table 9-7. Although the inositol phosphatides have not yet been adequately characterized, it appears that only partially phosphated inositols, such as the *m*-diphosphate, occur in the phosphatides.

Another group of glycerophosphatides which are quite analogous to the phosphatidyl esters are the plasmalogens or acetal phosphatides (see Table 9-8). A recently crystallized representative of the group has been shown to be an acetal of α-glycerylphosphorylethanolamine. The sphingolipids are the class of lipids incorporating the base sphingosine. The zwitter-ion formula of one of these, sphingomyelin, is shown in Table 9-8.

By oxidation of a terminal alcohol of either of the glycerophosphates, one obtains the phosphoglyceric acids of which there are two forms: 3-phosphoglyceric acid, which is the oxidation product of α-glycerophosphoric acid and 2-phosphoglyceric acid, which is the oxidation product of

[258] M. C. Pangborn, *J. Biol. Chem.*, **168**, 351 (1947).

β-glycerophosphoric acid. In the case of the phosphoglyceric acids, both varieties have optically active isomers. Conversion from the 3-form to the 2-form is relatively rapid and presumably occurs through a mechanism involving a cyclic intermediate similar to the one shown in Table 9-8 for the α- to β-glycerophosphoric acid interconversion. This step, which is labeled 1 in equation 9-30, is catalyzed by one of the transphosphorylating enzymes listed in Table 9-11, pages 595–598.



(9-30)

The equilibrium constant for the interconversion between the two phosphoglyceric acids is given below.[259]

K_1 = 2-phosphoglyceric acid/3-phosphoglyceric acid =

0.2 at 20°C. (9-31)

By removing a mole of water from 2-phosphoglyceric acid, enol pyruvic phosphoric acid is formed, as shown in equation 9-30. This is, again, an equilibrium reaction with the equilibrium constant being given below.

K_2 = enol pyruvic phosphoric acid/2-phosphoglyceric acid =

2.9 at 24°C. and 2.7 at 20°C. (9-32)

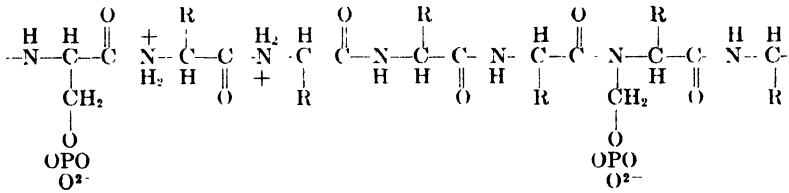
The equilibrium between 2-phosphoglyceric acid and enol pyruvic phosphoric acid is catalyzed by a specific enzyme called enolase. This enzyme has been obtained in crystalline form[259] and is a protein having a molecular weight of 66,000. The enzyme is inactive unless there are some magnesium, manganese, or zinc ions present in the solution. The action of enolase is inhibited by fluoride through some kind of an interaction of the fluoride ion with phosphate or arsenate ion, magnesium ion, and the enolase protein.

Another interesting class of naturally occurring orthophosphates is the

[259] O. Meyerhof, *The Enzymes*, eds. J. B. Sumner and K. Myrbäck, Academic Press, New York, 1951, Vol. 1, Part 2, Chapt. 39, pp. 1207–16.

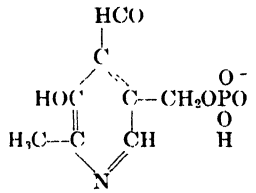
[260] G. E. Perlmann, *Phosphorus Metabolism*, ed. by W. D. McElroy and B. Glass, The Johns Hopkins Press, Baltimore, 1951, Vol. II, pp. 167–85; "Nucleic Acids and Nucleoproteins," Cold Spring Harbor Symposia, *Quant. Biol.*, **12**, 1 (1947)

phosphoproteins,[260,261] a common example of which is found in casein.[261] Up to the present time, no phosphoprotein has been isolated as a single, crystalline entity. However, casein has been carefully investigated by both physical and chemical means,[261] and it is known to consist of several species, some of which can polymerize. Known phosphoproteins are mixtures, and their classification is based entirely on the fact that, in contrast to the nucleoproteins, they lack purine and pyrimidine bases and contain phosphoric acid esterified to an amino acid. The phosphate group in the phosphoproteins is relatively stable in acid but is easily hydrolyzed in 0.25 *N* sodium hydroxide at 37°C. The available evidence indicates that the phosphoric acid is esterified with the hydroxyl group of serine and perhaps of threonine in the phosphoproteins. A diagrammatic representation of a segment of a phosphoprotein chain is given below:



(9-33)

There are a number of miscellaneous organic orthophosphates of biological interest which have not been discussed in the above paragraphs. One of these is the coenzyme, pyridoxal phosphate, the structure of which is shown below.[262] Pyridoxal, which is vitamin B_6, is phosphorylated in the organism to give this coenzyme for amination and decarboxylation of keto and amino acids.



pyridoxal-5-phosphate

(9-34)

[261] P. H. von Hippel and D. F. Waugh, *J. Am. Chem. Soc.*, **77**, 4311 (1955); *ibid.*, **78**, 4576 (1956); R. C. Warner, *J. Am. Chem. Soc.*, **66**, 1725 (1944). Also see W. O. Ware and H. O. Wyles, *Encyclopedia of Chemical Technology*, eds. R. E. Kirk and D. F. Othmer, Interscience Publishers, New York, 1949, Vol. 3, pp. 225–37; H. Eilers, R. N. J. Saal, and M. van der Woarden, *Chemical and Physical Investigations on Dairy Products*, Elsevier Publishing Co., Amsterdam, 1947, Chapt. II.

[262] E. A. Peterson and H. A. Sober, *J. Am. Chem. Soc.*, **76**, 169 (1954). Also see I Gunsalus, *Phosphorus Metabolism*, eds. W. D. McElroy and B. Glass, The Johns Hopkins Press, Baltimore, 1951, Vol 1, pp 417–20.

Properties of the Organic Orthophosphates

The detailed crystal structure of dibenzyl phosphate has been studied by x-ray diffraction.[263] In this compound, $(C_6H_5CH_2O)_2PO(OH)$, three of the P-O distances are about equal to the usual P-O atom-center length of 1.55 A., and the fourth P-O distance to the isolated oxygen atom is shorter, being 1.47 A. Thus, three P—O bonds exhibit 0.3 π-bond per σ-bond, and the fourth one exhibits 0.7 π-bond per σ-bond, so that the PO_4 group has about 1.6 π-bonds in all. The C-O distances are 1.46 A., which is somewhat larger than the accepted σ-bond distance. The C–O–P bond angle is 120°, and the smallest O–P–O angles of 104° lie between the two ester oxygens and between one ester oxygen and the OH group. The largest ∠ OPO value is 117°, corresponding to the angle between the OH group and the isolated oxygen atom.

The simple trisubstituted orthophosphate esters (trialkyl, triaryl, or mixed aryl alkyl) are very similar to the esters of organic acids, in that they usually can be distilled under reduced pressure without excessive decomposition and are soluble in a large number of organic solvents. The trialkyl orthophosphates of moderately low molecular weight are liquids with the typical ethereal odor of esters. A few per cent of any orthophosphate ester containing alkyl group(s) undergoes thermal decomposition in 24 hr. at 150°C., although the same ester is indefinitely stable at room temperature. Thermal decomposition is acid-catalyzed and proceeds by the splitting off of an unsaturated aliphatic hydrocarbon.[264] This indicates that the weakest point of the molecule with respect to thermal decomposition is the oxygen-aliphatic carbon bond. When both hydrogens on the number-two carbon atom of the aliphatic group are replaced by alkyl groups, the rate of thermal decomposition is considerably reduced, since the formation of a 1-alkene hydrocarbon can no longer proceed by the usual process, the equation for which is given below:

$$\begin{array}{l} C_6H_5 \\ O \\ RCH_2CH_2OPO \\ O \\ C_6H_5 \end{array} \xrightarrow{\Delta} RCH=CH_2 + \begin{array}{l} C_6H_5 \\ O \\ HOPO \\ O \\ C_6H_5 \end{array} \qquad (9\text{-}35)$$

Phosphate esters (such as the triaryl phosphates) in which the above reaction cannot take place also undergo thermal decomposition, but the rate is five to ten times slower. As compared to the neutral esters, the acid orthophosphates decompose much more rapidly on heating. Thus, a

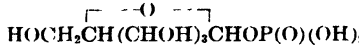
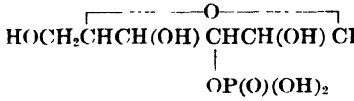
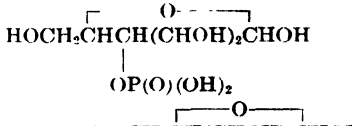
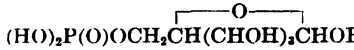
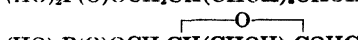
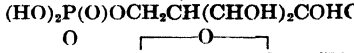
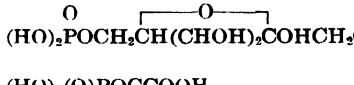
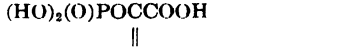
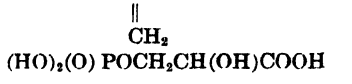
[263] J. D. Dunitz and J. S. Rollett, *Acta Cryst.*, **9**, 327 (1956).

[264] H. R. Gamrath, R. E. Hatton, and W. E. Weesner, *Ind. Eng. Chem.*, **46**, 208 (1954).

TABLE 9-9
Some Physical Properties of Orthophosphate Esters

Name	Formula	Specific gravity	Melting or boiling point (°C.)	Index of refraction (n_D^{25})	Solubility in water	Remarks
Monomethyl phosphate	$CH_3OP(O)(OH)_2$		Decomp.		Miscible	
Dimethyl phosphate	$(CH_3O)_2P(O)(OH)$		Decomp.		Very sol.	Lead salt, m.p = 155°C.
Trimethyl phosphate	$(CH_3O)_3PO$	$1.197_0^{22°}$	197° (b.p.)	1.3950	1:1 at 25°	
Monoethyl phosphate	$(C_2H_5O)P(O)(OH)_2$		Decomp		Miscible	
Diethyl phosphate	$(C_2H_5O)_2P(O)(OH)$	$1.175_4^{0°}$	203° (b.p.)	1.415	Very sol.	Lead salt, m.p = 180°C.
Triethyl phosphate	$(C_2H_5O)_3PO$	$1.064_4^{25°}$	215° (b.p.)	1.4039	1.1 at 25°	
Monophenyl phosphate	$(C_6H_5O)P(O)(OH)_2$		99° (m.p.)			
Diphenyl phosphate	$(C_6H_5O)_2P(O)(OH)$	$1.242_{25}^{60°}$	70° (m.p.)		3.100	Dihydrate, m.p. = 51°C.
Triphenyl phosphate	$(C_6H_5O)_3PO$	$1.206_4^{58°}$	50° (m.p.)		Insol	

TABLE 9-10 Apparent Ionization Constants[a] of Some Orthophosphate Derivatives

Compound	Formula	pK_1	pK_2	pK^b
Orthophosphoric acid	$OP(OH)_3$	1.97	6.82	12
Monomethyl phosphate	$(CH_3O)(O)P(OH)_2$	1.54	6.31	
Monoethyl phosphate	$(C_2H_5O)(O)P(OH)_2$	1.60	6.62	
Mono-*n*-propyl phosphate	$(n\text{-}C_3H_7O)(O)P(OH)_2$	1.88	6.67	
Mono-*n*-butyl phosphate	$(n\text{-}C_4H_9)(O)P(OH)_2$	1.89	6.84	
Dimethyl phosphate	$(CH_3O)_2(O)POH$	1.29	-	
Diethyl phosphate	$(C_2H_5O)_2(O)POH$	1.39	-	
Di-*n*-propyl phosphate	$(n\text{-}C_3H_7O)_2(O)POH$	1.59	-	
Di-*n*-butyl phosphate	$(n\text{-}C_4H_9O)_2(O)POH$	1.72		
α-Glycerophosphoric acid	$HOCH_2CH_2(OH)CH_2OP(O)(OH)_2$	1.40	6.44	-
β-Glycerophosphoric acid	$(HOCH_2)_2CHOP(O)(OH)_2$	1.37	6.34	
Glyceraldehyde phosphoric acid	$OCHCH_2(OH)CH_2OP(O)(OH)_2$	2.10	6.75	
Dihydroxyacetone phosphoric acid	$HOCH_2COCH_2OP(O)(OH)_2$	1.77	6.45	
Glucose-1 phosphate		1.10	6.13	-
Glucose-3 phosphate		0.84	5.67	-
Glucose-4 phosphate		0.84	5.67	-
Glucose-6 phosphate		0.94	6.11	—
Fructose-6 phosphate		0.97	6.11	
Fructose-1,6 phosphate		1.48	6.32	--
Enol-pyruvic phosphoric acid		ca. 1	6.38	3.5
3-Phosphoric glyceric acid		1.42	5.98	3.42
2,3-Diphosphoric glyceric acid		ca. 1	7.46 7.99	ca. 3.5

[a] These constants are not corrected for activities and hence are only apparent values.

[b] This pK refers to the organic acid.

mixture of monoethyl and diethyl phosphates was found to decompose upon heating to give first alcohol, then ethylene, and finally triethyl phosphate as distillates, leaving a residue of the acid esters of condensed phosphoric acids.[265] The mono- and dialkyl orthophosphates are very soluble in water,[244] and salts of these partial esters can be prepared by simply neutralizing with the appropriate base. The salts usually have low melting points (below several hundred degrees) as compared to the completely inorganic phosphates. Some physical data on several orthophosphate esters are given in Table 9-9.

The single hydrogen of the diesters of orthophosphoric acid is strongly dissociated, having an ionization constant approximately equal in magnitude to K_1 of orthophosphoric acid. The monosubstituted orthophosphate esters have two acid hydrogen atoms with ionization constants approximately equal to K_1 and K_2 of orthophosphoric acid These ionization constants[266] are listed in Table 9-10, where it can be seen that monomethyl phosphate is a stronger acid than unesterified phosphoric acid, and that, as the size of the alkyl group is increased, the mono- and diesters become slightly weaker acids. The strongest acids of all of the compounds listed in Table 9-10 are the hexose-3,4, and 6-phosphates The unusually strong ionzation of the first acid hydrogen in these compounds has been attributed to the formation of a hydrogen bond between the bridging oxygen of the sugar moiety and an oxygen of the PO_4 group by use of the second acid hydrogen of the phosphate, as shown in Table 9-7

The acyl phosphates, such as acetyl phosphate, serve as good acylating agents. The kinetics of the acetylation of amines and amino acids by acetyl phosphate has been studied.[247] This work is of especial interest to biologists because it is a way of synthesis for peptide bonds

Interchange Reactions of Organic Orthophosphates

In the chemistry of esters of organic acids, displacement reactions,[267] otherwise called ester interchange reactions, are very common. Thus, such

[265] C. A. Hochwalt, J. H. Lum, J. E. Malowan, and C. P. Dyer, *Ind. Eng. Chem.*, **34**, 20 (1942).

[266] W. D. Kumler and J. J. Eiler, *J. Am. Chem. Soc.*, **65**, 2355 (1943); W. Kiessling, *Biochem. Z.*, **273**, 103 (1934); O. Meyerhof and K. Lohmann, *ibid.*, **185**, 113 (1927); H. Wassermeyer, *Z. physiol. Chem.*, **179**, 228 (1928); C. Cori, S. Colowick, and G. Cori, *J. Biol. Chem.*, **121**, 465 (1937).

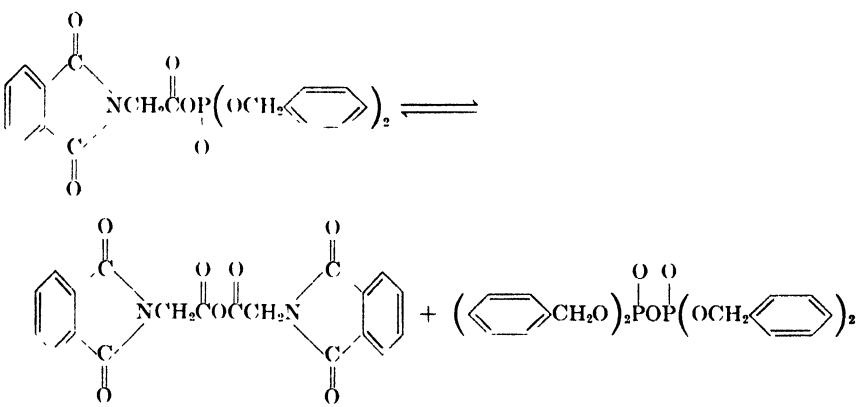
[267] G. Calingeart and H. A. Beatty, *Organic Chemistry*, ed. H. Gilman, 2nd ed., John Wiley & Sons, Inc., New York, 1943, Vol. 2, Chapt. 24, pp. 1806–20; R. C. Fuson, *Advanced Organic Chemistry*, John Wiley & Sons, Inc., New York, 1950, p. 201; P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 87–91, 320–21, 339.

mixtures as ethyl acetate plus propyl butyrate undergo interchange (in the presence of acid catalysts and high temperatures to speed up the reaction) to give some ethyl butyrate and propyl acetate. A related process is the alcoholysis of esters of organic acids in which the alcohol group of the ester interchanges with another alcohol. Similarly, esters of organic acids readily undergo acidolysis, which is also a type of displacement reaction.

Such reactions occur for the orthophosphate esters, but the rate is much slower. In fact, the rate is so slow in the case of the orthophosphate esters of monohydroxyl alcohols that a number of organic chemists have said that the reaction does not occur! That exchange is not free and rapid, even in fairly acid media, is indicated by the extractive separation[268] of RH_2PO_4 and R_2HPO_4. This is also borne out by the separation of phosphate esters through distillation. In the alcoholysis of trialkyl phosphates,[269] there is an interesting side reaction whereby ethers are formed in rather large quantities.

Obviously, the isomerization reactions whereby α-glycerophosphate goes into the β-form and 2-phosphoglyceric acid goes into 3-phosphoglyceric acid are special types of interchange reactions, exhibiting rapid rates because of the bridging mechanism discussed previously.

Related to ester interchange are the processes whereby mixed acid anhydrides form anhydrides of each pure acid, and acid anhydrides react with acids. Organic acid anhydrides exhibit this behavior, and the interchange occurs at quite a rapid rate Although there are not many data available,



(9-36)

[268] D. C. Stewart and H. W. Crandall, *J. Am. Chem. Soc.*, **73**, 1377 (1951).

[269] W. H. C. Rueggeberg and J Chernack, *J. Am. Chem Soc.*, **70**, 1802 (1948); A. D. F. Toy, *ibid.*, **66**, 499 (1944).

it appears that this type of interchange also occurs readily in the case of acyl phosphates. Thus, for example, the preceding disproportionation reaction[270] is found to go upon attempted recrystallization of the mixed anhydride from benzene or upon addition of a small amount of triethylamine to the molten mixed anhydride.

Hydrolysis of C—O—P Linkages

The monoesters of orthophosphoric acid have been found [271-273] to hydrolyze most rapidly at pH values near 4, as shown in Figure 9-29. In basic media, these esters are extremely stable, and no hydrolysis has ever

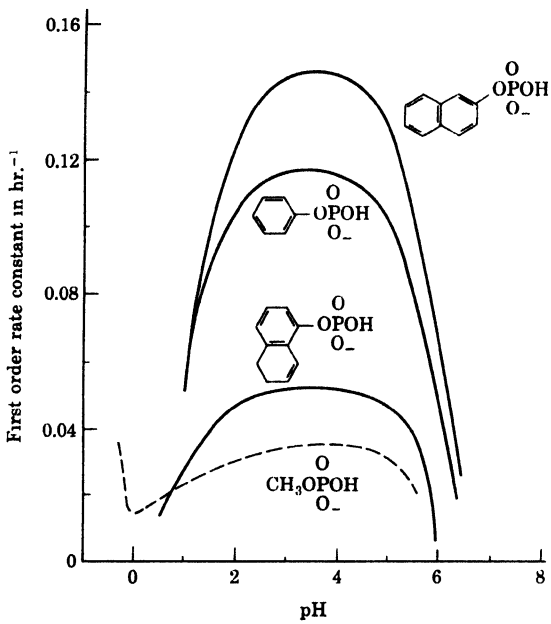


Fig. 9-29. The over-all rate of hydrolysis of several monoesters of phosphoric acid at 80°C.

[270] J. C. Sheehan and V. S. Frank, *J. Am. Chem. Soc.*, **72**, 1312 (1950).

[271] J. D. Chanley, E. M. Grindler, and H. Sobotka, *J. Am. Chem. Soc.*, **74**, 4347 (1952); J. D. Chanley and E. M. Grindler, *ibid.*, **75**, 4035 (1953); J. D Chanley and E. Feageson, *ibid.*, **77**, 4002 (1955).

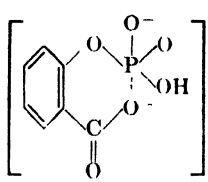
[272] P. W. C. Barnard, C. A. Butnon, D. R. Llewellyn, K. G. Oldham, B. L. Silver, and C. A. Vernon, *Chemistry & Industry*, **1955**, 760.

[273] A. Desjobert, *Bull. soc. chim. France*, **14**, 809 (1947); R. H. A. Plimmer and W J N. Burch, *J. Chem. Soc.* **1929**, 279.

been observed. Likewise, they are also quite stable in strong acid. This has been explained[272] by assuming that the singly charged form, $ROP(O_2^-)(OH)$, is the most labile, whereas the fully ionized species, $ROPO_3^{2-}$, is most stable, and the un-ionized form, $ROP(O)(OH)_2$, is relatively stable toward hydrolysis. In strongly acid solutions there is a significant increase in the rate of hydrolysis[272] (*e.g.*, on going from 1 *N* to 5 *N* HCl, the rate increases 4.5-fold for monomethyl phosphate). This indicates that the hydrolysis of the unionized form, $ROP(O)(OH)_2$, is acid catalyzed.

Tracer studies[272] show that the P—O bond in monomethyl phosphate undergoes scission in the neutral region, whereas in the presence of strong acids both the C—O and P—O bonds in the C—O—P linkage are split during hydrolysis. For the glycerophosphates and for monophenyl and mono-*p*-tolyl phosphates in strong acid, the P—O bond, rather than the C—O bond, undergoes scission during hydrolysis. The same isotopic tracer experiments which gave this information also showed that phosphate migration back and forth from terminal positions to the middle position in the glycerophosphate is considerably faster than hydrolysis, and that both processes occur solely by steps involving scission of P—O bonds. The evidence is consistent with the formation of a cyclic intermediate,[267] such as the one shown in Table 9-7. Both the hydrolysis in strong acid and the intramolecular migration are acid catalyzed.

It is found[271] that the rate of hydrolysis of mono-*o*-carboxyaryl phosphates is very fast as compared to simple monoaryl phosphates or to monocarboxyaryl phosphates in which the carboxyl group is in the meta or para position. This rapid hydrolysis has been attributed to the transition complex shown below for phosphoryl salicylate, which can, and presumably does, form an acyl phosphate, the C—O—P linkage of which is considerably less stable than the C—O—P linkage in a phosphate ester.



activated complex (9-37)

These mono-*o*-carboxyaryl phosphates exhibit the same general type of variation of hydrolysis rate with pH that is shown in Figure 9-29. In other words, the rate of hydrolysis for these compounds is greatest in the neutral region.

Unlike the mono- and dialkyl phosphates, which are exceedingly stable

in alkaline solution, the trialkyl esters undergo hydrolysis at quite a fast rate in alkali. Only one alkyl group is removed in this reaction, since the dialkyl phosphate is very stable in alkaline solution. In neutral or acid solutions, the mono-, di-, and trialkyl esters hydrolyze at rates which are not very different from each other. Presumably, the trialkyl phosphate hydrolyzes slightly slower than the dialkyl phosphate, which in turn hydrolyzes somewhat slower than the monoalkyl phosphate, since there is some build-up of the mono- and dialkyl derivatives during hydrolysis of the trialkyl phosphate. From the few data available,[272] it appears that hydrolysis of trimethyl phosphate is both acid and base catalyzed. Tracer experiments show that in the hydrolysis of trimethyl phosphate, O—P scission occurs in alkaline solution,[274] whereas O—C scission occurs in acid or neutral solutions.

One might postulate that the relatively rapid degradation of trialkyl orthophosphates as compared to the mono- or dialkyl derivatives is due to the three covalent bonds to the PO_4 group causing a loss of π-bond resonance between the four P—O bonds (see pp. 437–441). This explanation would be in accord with the pictures presented for the hydrolytic degradation of P_4O_{10} (pp. 393–396), crosslinked Kurrol's salt (pp. 676–677), and tetraalkyl pyrophosphate (pp. 632–633). The whole question of hydrolytic scission of C—O—P linkages in organic phosphates is worthy of considerably more study than it has received to date. Information about the kinetics of this process is particularly important to an understanding of many biological phenomena.

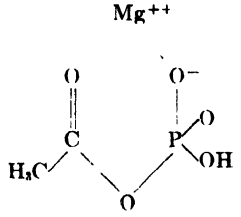
The activation energy for the hydrolysis of monoaryl orthophosphates,[271] whether or not there is a carboxyl group in the ortho position, ranges from 24 to 30 kcal./mole—values which are very similar to those obtained for the hydrolytic scission of P—O—P linkages in the condensed phosphates (pp. 452–458). However, an activation energy as low as 4 kcal. has been reported[275] for the hydrolysis of tris-*p*-nitrophenyl phosphate, $OP(OC_6H_4NO_2)_3$ in both basic and neutral solutions. Such low activation energies for orthophosphate ester hydrolysis generally seem to be associated with the *p*-nitrophenyl group. Presumably, the strong electron-accepting tendency of this group removes electrons from the PO_4 tetrahedron and, perhaps by reducing π-bonding, weakens the tetahedron so as to make *d*-orbitals of the phosphorus more readily available for bonding to a fifth oxygen in the activated complex.

[274] E. Blumenthal and J. M. Herbert, *Trans. Faraday Soc.*, **41**, 611 (1945).

[275] J. A. A Ketelaar, H. R. Gersmann, and K. Koopmans, *Rec. trav. chim.*, **71**, 1253 (1952); J. A. A. Ketelaar, *ibid.*, **69**, 649 (1950).

Acetyl phosphate, which exemplifies the mixed anhydrides of organic acids and orthophosphoric acid, hydrolyzes very rapidly as compared to the orthophosphate esters. When considering acid anhydrides, it is seen that acetyl phosphate, which has a half-life of several hours in water at room temperature, is considerably more stable than acetic anhydride, the half-life of which is only a few seconds under the same conditions. However, the P—O—P linkage in the condensed phosphates (which also can be considered as acid anhydrides) has a half-life of the order of magnitude of decades to centuries under the same experimental conditions (see Chapt. 8). The few data[276] available on hydrolytic degradation of acetyl phosphate indicate that there is strong acid catalysis, as well as strong basic catalysis, so that the slowest rate of hydrolysis is observed in the neutral region, pH 5 to pH 9.

In addition to acid and base catalysis, organic bases, such as pyridine and aniline, act as catalysts even in buffered solutions, where they can have no effect on the pH. Catalysis by pyridine is undoubtedly due to the formation of an acetylpyridinium ion, so that the entire mechanism of the hydrolysis process is changed. In the absence of pyridine at pH 7, cleavage of the P—O bond occurs with displacement of acetate. At the same pH, the pyridine-catalyzed reaction involves a C—O scission with displacement of the phosphate. Thus, in the normal hydrolysis, acetylphosphate acts as a phosphorylating agent, whereas, in the presence of pyridine, it serves as an acetylating agent. Pyridine must be classed as a mildly effective catalyst, since rather large concentrations of pyridine increase the reaction rate by a relatively small factor, about two. It should also be noted that magnesium ion has been shown to increase the rate of hydrolysis by a factor of approximately two in the neutral pH region. This catalysis has been attributed[276] to the formation of a chelate ring, as shown below



(9-38)

In the neutral region, the hydrolysis of acetylphosphate proceeds by scis-

[276] D. E. Koshland, *J. Am. Chem. Soc.*, **74**, 2286 (1952); *A Symposium on Phosphorus Metabolism*, eds. W. D. McElroy and B. Glass, Johns Hopkins Press, Baltimore, 1951, Vol. 1, pp. 536–46; R. Bentley, *J. Am. Chem. Soc.*, **71**, 2765 (1949).

sion of the P—O bond, whereas, in the basic region of pH, the process involves scission of the C—O bond.

The thermodynamics of the hydrolysis of organic orthophosphates has been of considerable interest to biologists.[277] The standard free energy of hydrolysis, ΔF (based on the activity of water and total activities of each substance rather than the activity of any particular ion), of the phosphate monoesters is relatively small, ranging from 2.2 kcal. for α-glycerophosphate to 4.9 kcal. for glucose-1-phosphate at 38°C. and pH 8.5. These are all "low-energy phosphate bonds." However, the C—O—P linkages in mixed acid anhydrides are "high-energy phosphate bonds"[277] with standard free energies of hydrolysis around 15–16 kcal. at 38°C. and pH 8.5. This is also true of enol pyruvic phosphate, in which there is a $=CH_2$ attached to the carbon of the C—O—P linkage as compared to the =O on this carbon in the case of mixed acid anhydrides.

The heat of hydrolysis (ΔH at pH 7) for α-glycerophosphate is 1.3 kcal. as compared to values of 8.5 kcal. and about 8 kcal. for enol pyruvic phosphate and acetyl phosphate, respectively. It is interesting to note that *p*-nitrophenyl phosphate (the low activation energy for the hydrolysis of which was mentioned previously) has a heat of hydrolysis of 4.5 kcal., which is high for a simple phosphate monoester. Of course, *p*-nitrophenol is an acid of medium strength, and its phosphate can be considered as being somewhat intermediate between the esters and acid anhydrides.

The free-energy data show that there is a detectable equilibrium between the unhydrolyzed orthophosphate esters and the hydrolysis products, whereas in the case of the mixed acid anhydrides the equilibrium is so far toward the hydrolysis products as to represent complete hydrolysis for all practical purposes in moderately dilute solutions. Obviously, hydrolytic scission of a C—O—P linkage in a mixed anhydride gives off about six times as much heat as the hydrolysis of a C—O—P linkage in a phosphate ester.

Enzymes Acting on C—O—P Linkages

A large number of enzymes are known which catalyze the scission or formation of C—O—P linkages in orthophosphates. Examples of these

[277] For example, P. Oesper, *Symposium on Phosphorus Metabolism*, eds. W. D. McElroy and B. Glass, Johns Hopkins Press, Baltimore, 1956, Vol. 1, pp. 523–36. N. O. Kaplan, *The Enzymes*, eds. J. B. Sumner and K. Myrback, Academic Press, New York, 1951, Vol. II, Part 1, Chapt. 45, pp. 55–113. Also see H. Kalckar, *Chem. Revs.*, **28**, 71 (1941), F. Lipmann, *Advances Enzymol.*, **1**, 99 (1941); *ibid.*, **6**, 243 (1946).

enzymes are given in Table 9-11. In the general class of phosphatases[278] there are three major subgroups: the phosphomonoesterases, which catalyze hydrolytic scission of C—O—P linkages in phosphate esters; the phosphodiesterases, which catalyze the hydrolysis of only one C—O—P linkage in a diester; and the phosphoacylases, which catalyze the hydrolysis of C—O—P linkages in mixed acid anhydrides of orthophosphoric acid. As shown in Table 9-11, some of the phosphatases appear to be quite specific although, as a class, the phosphatases have a reputation among enzymologists of being unusually nonspecific. It is interesting to note that, in the presence of high concentrations of various alcohols, the phosphatases catalyze alcoholysis[279] instead of hydrolysis reactions. In such cases, the phosphatases are acting as transphosphorylases.

The phosphorylase enzymes catalyze the reversible reactions whereby saccharides (or nucleosides) plus orthophosphate form sugar phosphates.[280] This type of reaction occurs by scission of terminal glycosidic linkages in the polysaccharide to give a saccharide chain, which is shorter by one sugar unit, plus this sugar as a phosphate. Equilibrium can be achieved from either end of the reaction. If one starts with pure polysaccharide plus inorganic orthophosphate, there is no need to have any sugar phosphate originally present in order to have the enzyme function. However, when starting with pure sugar phosphate, there must be a trace of polysaccharide originally present in order for more polysaccharide to form.

Arsenate ion can substitute for the orthophosphate ion in the breakdown of starch by phosphorylase. In this case, there is no accumulation of a sugar phosphate, but the starch is converted entirely to the sugar. Presumably, there is formation of an intermediate sugar arsenate which is so unstable that it immediately decomposes to sugar plus arsenate. Similarly, substitution of arsenate for phosphate in the presence of sucrose phosphorylase can cause the hydrolytic decomposition both of sucrose and of glucose-1-phosphate. This postulated rapid hydrolytic scission of As—O—C linkages is similar to the fast scission of As—O—P linkages described on pages 793 and 678.

The transphosphorylating enzymes are the third class of enzymes involved in scission or formation of C—O—P linkages.[281] As the name

[278] J. Roche, *The Enzymes*, eds. J. B. Sumner and K. Myrbäck, Academic Press, New York, 1950, Vol. 1, Part 1, Chapt. 11, pp. 473–510.

[279] H. Green and O. Meyerhof, *Federation Proc.*, **9**, 179 (1950); J. Appleyard, *Biochem. J.*, **42**, 596 (1948); B. Axelrod, *J. Biol. Chem.*, **172**, 1 (1948); **176**, 295 (1948).

[280] W. Z. Hassid, M. Doudroff, and H. A. Barker, *The Enzymes*, ed. J. B. Sumner and K. Myrbäck, Academic Press, New York, 1950, Vol. 1, Part 2, Chapt. 31, pp. 1014–39.

[281] S. P. Colowick, *The Enzymes*, eds. J. B. Sumner and K. Myrbäck, Academic Press, New York, 1950, Vol. 2, Part 1, Chapt. 46, pp. 114–50.

TABLE 9-11
Known Enzymes for Scission or Formation of C—O—P Linkages in Orthophosphates

Class	Enzyme	Reaction catalysed	Optimum conditions and inhibitions	Chief sources	Remarks
Phosphatases					
Phosphomonoesterases	Phosphomonoesterase—Type I	Hydrolysis of phosphate esters to the inorganic orthophosphate	pH: 8.6–9.4. Mg^{2+} activation. —SH inhibition	Bone; kidney, intestinal mucosa; mammary glands	Purified but not crystallized. Catalytic action on a class of reactions—not specific to certain reactants but will not catalyse phytic acid hydrolysis
	Phosphomonoesterase—Type II	As above	pH: 5.0–5.5. F^- inhibition. Mg^{2+} gives no action	Liver; seeds; fungi, prostate	As above
	Phosphomonoesterase—Type III	As above	pH: 3.4–4.2. Mg^{2+} inhibition	Liver; top yeasts	Impure and nonspecific
	Phosphomonoesterase—Type IV	As above	pH: 5.0–6.0. Mg^{2+} activation	Red blood cells, bottom yeasts	Impure and nonspecific. Differentiated from type I by faster action on α- than on β-glycerophosphate. Reverse is true for types I–III
	Phytase Type I	Phytic acid[a] → inositol +6 inorganic orthophosphate	pH: 7.8. Mg^{2+} activation	Rat intestine	Will also catalyse hydrolysis of other orthophosphate esters. Not purified[a]

	Phytase Type II	As above[a]	pH: 5.5. Mg^{2+} gives no action	Mustard, soybean, and cereal seeds	As above[a]
	Hexosediphosphatase	1,6 fructosediphosphate hydrolysis		Liver; kidney; yeasts	May be specific, more work needed. Impure
	5-Nucleotidase	Hydrolyses adenosine-5 monophosphate and inositol-5 monophosphate	Slightly alkaline pH. Mg^{2+} has no effect	Retina; nerves; prostate; testes; sperm	Does not hydrolyse adenosine-2 monophosphate and various sugar phosphates
Phosphodiesterases	Phosphodiesterase—Type I	Hydrolysis of only one C—O—P link in a diester	pH. 8.5–9.0	Venoms; serum	Not purified. Prostate and citrus fruit are devoid of diesterase activity
	Phosphodiesterase—Type II	As above	pH: ca. 5.5	Rice bran; takadiase	As above. Perhaps also a Type III active at more acid pH
	Ribonuclease	Hydrolyses ribonucleic acid without liberating inorganic phosphate	pH: 7.7 and 60°C. No specific inhibitors	Pancreas; liver, spleen; lungs; & polymorphonuclear leucocytes	Crystalline enzyme with mol. wt. of 15,000. An albumin type of simple protein. Does not affect desoxyribonucleic acid
	Desoxyribonuclease	Hydrolyses desoxyribonucleic acid without liberating inorganic phosphate	pH: ca. 7.0 & ca 37°C. Mg^{2+} activation at 3 p.p.m. Inhibition by F^-, Cl^-, & arsenate. Also by a specific protein	Pancreas and other organs	Crystalline enzyme. All organic phosphorus is made acid soluble by action of this enzyme on desoxyribonucleic acid
	Desoxypentosenuclease	Hydrolyses desoxypentosenucleic acid without liberating inorganic phosphate	pH below 6.2	Yeast	Not well characterized. Insol. in H_2O but soluble in salt solutions

(continued)

TABLE 9-11 (*continued*)

Class	Enzyme	Reaction catalysed	Optimum conditions and inhibitions	Chief sources	Remarks
Phospho-acylases	Phospho-acylase	Hydrolyses acetylphosphate and its homologs	Inhibited by many anions including orthophosphate	Muscles; other animal tissues	Not purified; but different from the phosphoesterases
Phospho-rylases	Polysaccharide phosphoryl-ase from muscle	Glycogen + inorganic orthophosphate = glucose-1-phosphate (only straight-chain glycogen or starch is involved)	pH affects equilib. of reaction which goes to the right with decrease in pH. Activated by adenylic acid. Inhibited by glucose, ammonium sulfate, & sodium 3-glycerophosphate	Rabbit skeletal muscle and other muscles	Crystalline enzyme in an *a* & *b* form. The *a* form is an euglobulin of mol. wt. 360,000 Resting muscles have high form *a*, fatigued muscles have high form *b*. Specific to glucose-1-phosphate
	Polysaccharide phosphoryl-ase from potato	Starch + inorganic orthophosphate = glucose-1-phosphate (only straight-chain glycogen or starch)	As above; but not activated or inhibited as stated	Potatoes and other plant tissues such as beans and peas	Not crystallized but purified
	"Q"-enzyme	As above but involves branched glycogen or starch by using α-1,6-glucoside linkages instead of α-1, 4 linkages		From plant or animal sources	Not well purified

	Sucrose phosphorylase	Sucrose + inorganic orthophosphate = glucose-1-phosphate + fructose	pH = ca. 7.0 Inhibited by free glucose	Bacteria, especially *Pseudomonas saccharophilia*	Enzyme formed only if the bacteria are given sucrose or raffinose as substrate. Specific action in mediating transfer of glucose from a disaccharide to a phosphate
Transphosphorylases[b]	Nucleoside phosphorylases	Nucleoside + inorganic orthophosphate = purine + sugar phosphate		Liver, spleen, & milk	Perhaps several enzymes in this class. None have been purified
Kinases	Yeast hexokinase	ATP[b] + hexose = hexose-6-phosphate + ADP	pH 8–9 (broad) Metal ion activated, especially with Mg^{2+}. Inactivated by mustard gas and trypsin Also inactivated by proteolytic enzymes. F^- has no effect. Inactivated when highly diluted in H_2O	Baker's yeast	Crystalline enzyme with mol. wt. of 96,600, phosphoprotein with 2 PO_4/molecule. Isoelectric point = pH 4.5–4.8 Specific for glucose, fructose, and mannose

(continued)

TABLE 9-11 (*continued*)

Class	Enzyme	Reaction catalysed	Optimum conditions and inhibitions	Chief sources	Remarks
	Mammalian hexokinases (fructokinase and others)	As above	pH 8 (for the enzyme from rat muscle.) Inhibition by pituitary hormones can be prevented by insulin	Variety of mammalian tissues, especially brain, liver, retina, heart, kidney, & skeletal muscle	Not purified. Probably a specific enzyme for fructose Not so stable as hexokinase from yeast Rapid loss of activity with pH at 6 or lower; also on dialysis
	Galactokinase	ATP + galactose = galactose-1-phosphate + ADP	pH 5.3–7.8 (optimum at 6) Mn^{2+}-activated	Brewer's yeast, liver Best source is *Saccharomyces fragilis*	Only partially purified Very specific. Only the terminal PO_4 of ATP[b] is transferred
	Phosphofructokinase	ATP + fructose-6-phosphate = ADP + fructose-1,6-phosphate	pH = ca. 6. Mg^{2+} activation necessary	Skeletal muscle, yeast, etc.	Partially purified. Specific. Perhaps a different enzyme converts fructose-1-phosphate to fructose-1,6-phosphate
	Phosphoglucokinase	ATP + glucose-1-phosphate = ADP + glucose-1,6-phosphate	pH = 6.8 Mg^{2+} or Mn^{2+}	Skeletal muscle and yeast	Hard to separate from phosphoglucomutase Partially purified Specific.
	3-Phosphoglycerokinase	1,3-Diphosphoglycerate + ADP = 3-phosphoglycerate + ATP	pH = ca. 6. Mg^{2+} activation	Muscle, tumor tissue, serum, & yeast. Enzyme is 0.2% by wt. in wet brewer's yeast	Crystalline. Specific. Kinetics have been thoroughly studied. One of the best understood enzymatic reactions

	Pyruvate-kinase	Phosphopyruvate + ADP = pyruvate + ATP	pH = 6.8. Both K^+ & Mg^{2+} are needed. Na^+ and Ca^{2+} have an antagonistic effect on the K^+ activation	Muscle & yeast	Crystalline. Specific. Kinetics has been well studied. Perhaps an additional enzyme for the reaction: Phosphopyruvate + ADP = pyruvate + AMP[b]
	Adenylate-kinase (Myokinase)	2 ADP = ATP + AMP[b]	pH = 7.5. Mg^{2+} activated, inactivated by oxidation but activity restored by —SH compounds	Skeletal muscle most; then heart, brain and finally liver. Also some in yeast	Well purified. Specific for adenine nucleotides. Enzyme can be boiled in 0.1N HCl without much loss of activity. Destroyed by digestion with pepsin
Mutases	Phosphoglucomutase	Glucose-1,6-phosphate + glucose-1-phosphate = glucose-6-phosphate + glucose-1,6-phosphate	pH = 7.5–9.2 (7.5 when Mg^{2+} is added). Active without metal ions but rate increased by Mg^{2+}, Mn^{2+}, & Co^{2+}. Deactivated by traces of heavy metals (Zn^{2+}, Cu^{2+}, Hg^{2+}, or Ag^+), therefore chelating agents cause activation. F^- inhibition	Skeletal muscle, liver, yeast, etc	Crystalline protein, showing single peak in electrophoresis. The glucose-1-phosphate = glucose-6-phosphate equilibrium reaction will not go without glucose-1,6-phosphate as coenzyme. Absolutely specific enzyme for the reaction shown

(continued)

TABLE 9-11 (*continued*)

Class	Enzyme	Reaction catalysed	Optimum conditions and inhibitions	Chief sources	Remarks
	Phosphoglyceromutase	3-Phosphoglycerate + 2,3-diphosphoglycerate = 2-phosphoglycerate + 2,3-diphosphoglycerate	Perhaps inhibited by doubly charged metal ions	Muscle and yeast	Not well purified
	Glucose-1-phosphate-transphosphorylase	2 Glucose-1-phosphate = glucose-1,6-diphosphate + glucose	pH = 5-6 (broad) Not activated by Mg^{2+} or other doubly charged metal ions	In microorganisms *E. coli*, *Aerobacter aerogenes*, or *Klebsiella pneumoniae*	Not purified

[a] Various ratios of mono-, di-, tri-, tetra-, and pentaorthophosphate derivatives of inositol are found for different preparations. Some monophosphoesterases will not catalyse the hydrolysis of phytic acid; whereas all phytases seem to catalyse hydrolysis of other esters.

[b] AMP = adenosine monophosphate, ADP = adenosine diphosphate, and ATP = adenosine triphosphate

"transphosphorylase" indicates, these enzymes are involved in processes where PO_4 groups are moved from one molecule to another or from one site to another in a given molecule. The two major subdivisions of this class are the kinases and mutases. The kinases catalyze those reactions in which the terminal PO_4 group of adenosine triphosphate (and perhaps other adenosine polyphosphates) is donated to a sugar or other hydroxy compound, or to an organic acid. The mutases accelerate the process whereby a phosphate group is moved from one position to another within a polyhydroxyl compound. The enzyme, glucose-1-phosphate transphosphorylase, catalyzes a reaction in which two moles of glucose-1-phosphate give one mole of glucose-1,6-diphosphate plus one mole of glucose. Again, this is a transfer of a phosphate group.[282] Like the phosphorylases, the transphosphorylases are involved in reactions in which a measurable equilibrium between product and reactant is found in dilute solution. On the other hand, the phosphatases usually catalyze reactions under conditions in which the equilibrium is shifted quite strongly toward the hydrolysis products.

[282] L. F. Leloir, R. E. Trucco, C. E. Cardini, A. C. Paladini, and R. Caputto, *Arch. Biochem.*, **24**, 65 (1949); also see, *ibid.*, **18**, 201 (1948); **19**, 339 (1948).

CHAPTER 10

Individual Chain Phosphates (Pyro-, Tripoly-, Tetrapoly-, and Pentapolyphosphates as Well as Kurrol's and Maddrell's Salts)

GENERAL HISTORY

Because of the great emphasis on the now obsolete ortho-pyro-meta classification of phosphates, the existence of members of the polyphosphate series (postulated by Fleitmann and Henneberg[1] in 1845) higher than the pyrophosphate have been disputed nearly up to the present time. Thus, the idea of tripolyphosphate as a crystalline entity[2–4] was not accepted until around 1940. Even after it was demonstrated that crystalline sodium tripolyphosphate appeared in the Na_2O–P_2O_5 phase diagram, many people would still not believe that there was a full family of polyphosphates. However, the considerable body of physical-chemical data[5] obtained in the decade starting with 1940 and the recent development of paper chromatography[6] in this field has proved, to even the most skeptical, that there is a homologous series of chain phosphates ranging from the monomer to the higher members which contain many thousands, and perhaps even millions, of phosphorus atoms in each separate anion. Although a number of the esters of the chain phosphoric acids have been prepared, the structures of only a few of them have definitely been demonstrated.

[1] T. Fleitmann and W. Henneberg, *Ann.*, **45**, 304, 387 (1845).

[2] H. Huber, *Z. angew. Chem.*, **50**, 323 (1937)

[3] K. R. Andress and K. Wust, *Z. anorg. u. allgem. Chem.*, **237**, 113 (1938); *ibid.*, **241**, 196 (1939).

[4] E. P. Partridge, V. Hicks, and G. V. Smith, *J. Am. Chem. Soc.*, **63**, 454 (1941).

[5] For a brief review, see C. F. Callis, J. R. Van Wazer, and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954).

[6] A. E. R. Westman and J. Crowther, *J. Am. Ceramic Soc.*, **37**, 420 (1954) is an example of the use of paper chromatography in assaying chain phosphates having as many as nine phosphorus atoms per chain; also see J. Crowther, *Anal. Chem.*, **26**, 1383 (1954)

CRYSTALLINE *VERSUS* AMORPHOUS COMPOSITIONS

In general, the chain phosphates appear between the ortho- (M_2O/P_2O_5 = 3) and metaphosphate (M_2O/P_2O_5 = 1) compositions. Although a large number of crystalline salts of the chain phosphates are known, there are many glassy and otherwise amorphous compositions which consist in great part of chain phosphates. The crystalline compositions which have been prepared to date correspond only to the lower members of the homologous series of chain phosphates and the extremely high members of the series. Thus, lead tetrapolyphosphate,[7] which exhibits a four-membered chain, is the largest of the short chain phosphates which has been crystallized from the melt. On the other hand, the extremely long chain phosphates, exhibiting hundreds and thousands of phosphorus atoms per chain,[8] are also made by crystallizing from the melt.

It is not surprising to find that the intermediate members of the homologous series of chain phosphates do not appear in crystalline form. Indeed, this appears to be the general case, which has been observed many times in the field of organic chemistry. One reason is that the longer members of an homologous series are usually not prepared and seldom occur as single entities. Rather, a distribution of molecular sizes is found which is difficult, if not impossible, to separate into the individual constituents. Since all of the members of such a mixture are rather similar, crystallization cannot proceed readily because the different sized members tend to substitute for each other in the growing crystal and thus stop the growth. In the case of mixtures of extremely long chain members of a given homologous series, this substitution of one member of the series for another during the growth of a crystal causes no great trouble, since the individual chains run through many unit cells in the crystal, and the exact length of the chain is no longer an important factor in determining the lattice parameters of the crystal.

Apparently, the practical molecular size limit above which crystals are difficult to form is also a function of the polarity of the units making up the molecule. Thus, a complete series of crystalline hydrocarbons going up to chain lengths of about 25 carbon atoms are known, whereas in the polyalcohol series, methyl alcohol readily crystallizes, ethylene glycol is harder

[7] R. K. Osterheld and R. P. Langguth, *J. Phys. Chem.*, **59**, 76 (1955); R. P. Langguth, R. K. Osterheld, and E. F. Karl-Kroupa, *ibid.*, **60**, 1335 (1956); also see R. P. Langguth, "A Study of Aggregation Reactions in Lead and Barium Phosphate Systems," M.S. Thesis, Cornell University, Ithaca, N Y., 1952; and M. Amadori, *Atti reale ist. veneto sci. lettere ed arti*, **76**, 419 (1916).

[8] H. Malmgren, *Acta Chem Scand*, **2**, 147 (1948); **6**, 1 (1952).

to crystallize, and glycerine crystals are a rare curiosity This points up a second factor which tends to set a practical upper limit to the size of molecules (or molecule-ions) which can be readily prepared in crystalline form. It is believed that the difficulty is due to improper aligning of the polypolar molecules, which strongly interact with their neighboring molecules during crystal growth. Moderately long, somewhat flexible, chains containing a series of polar groups can attach themselves to the growing crystal in an irregular manner so as to inhibit further growth.

The crystallization of the short chain sodium phosphates from water offers a very good example of the increasing difficulty to form crystals as the chain length increases. When dilute aqueous solutions of the sodium phosphates are treated with a relatively large volume of acetone or alcohol, the phosphate is precipitated. When a series of parallel experiments are run at equal P_2O_5 concentrations with (a) Na_2HPO_4, (b) $Na_4P_2O_7$, (c) $Na_5P_3O_{10}$, and (d) a solution of $Na_6P_4O_{13}$ obtained from alkaline cleavage of the sodium tetrametaphosphate, it is found that, on the addition of equal amounts of alcohol, (a) the orthophosphate is precipitated as a crystalline substance, (b) the pyrophosphate is precipitated as gummy crystals which in a short time solidify together into a hard mass due to crystal growth from the gummy phase, (c) the tripolyphosphate is precipitated as an oil which slowly transforms to crystals, and (d) the tetrapolyphosphate is precipitated as an oil which does not crystallize on standing. The crystallization of the tripolyphosphate from the precipitated, oily-looking liquid phase can be greatly speeded up by scratching the glass walls of the container with a glass rod; however, this technique and other common tricks for inducing crystallization do not seem to work on the sodium tetrapolyphosphate precipitated in this manner. Even in the case of the orthophosphate, it is possible to shock out the precipitate as an oil; on the other hand, it seems to be impossible to obtain the sodium tripoly- and tetrapolyphosphates in the form of crystalline material immediately upon adding a large volume of alcohol.

The two factors of (1) difficulty in crystallizing from mixtures of like substances and (2) the action of a series of polar groups on a molecule in inhibiting straightforward crystallization seem to explain the fact that chain phosphates in the range from 6 to about 200 phosphorus atoms have not yet been produced in crystalline form. The existence of reorganization processes in which there is a continuous break-up and re-forming of molecules from each other in melts probably does not change the picture of the situation depicted above. Indeed, such reorganization might well make it even more difficult to fit moderate-sized chains into a crystal lattice

forming from a melt. On the other hand, the reorganization probably helps the formation of long chain crystals from melts, with the crystals forming directly from the reorganizing parts.

POLYPHOSPHATE PHASE DIAGRAMS

The equilibria between crystalline solids and their respective melts in the range between the meta- and pyrophosphate compositions have been very carefully studied in the Na_2O-K_2O-P_2O_5 system. Although there were several preliminary investigations[9] of the phase equilibria of sodium

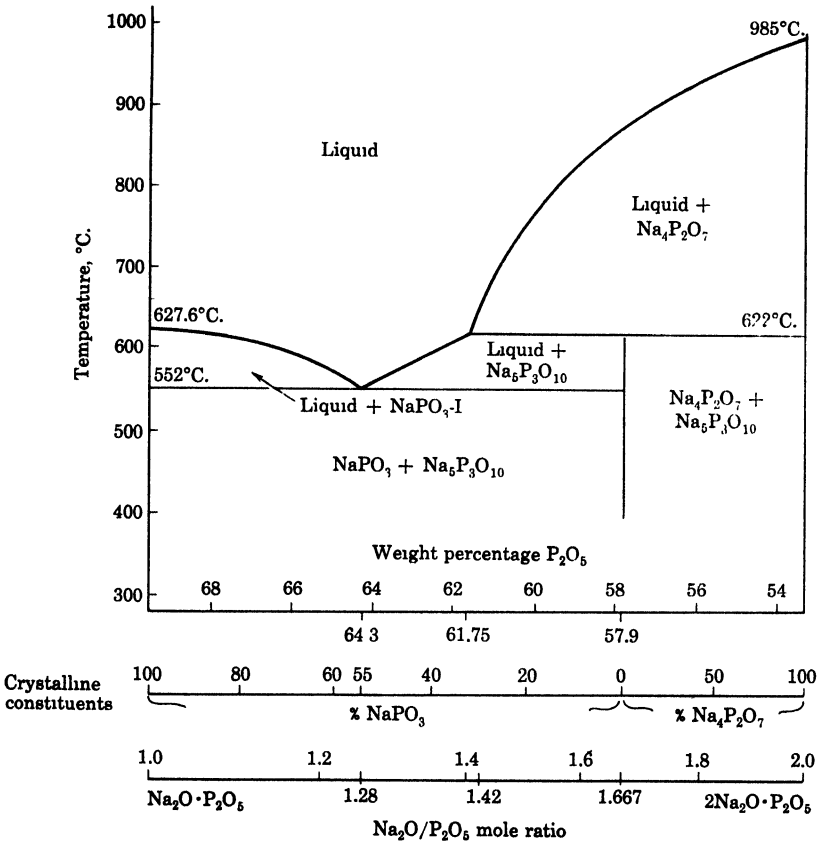


Fig. 10-1. The sodium phosphate phase diagram between $Na_2O \cdot P_2O_5$ and $2Na_2O \cdot P_2O_5$.

[9] For example N. Parravano and G. Calcagni, *Z. anorg. Chem.*, **65**, 1 (1910); P. Pascal, *Bull. soc. chim. France*, **35**, 1131 (1924); A. Boullé, *Compt. rend.*, **200**, 635, 832 (1935).

phosphate compositions lying between 2 $Na_2O \cdot P_2O_5$ and $Na_2O \cdot P_2O_5$, the first reliable data on the subject were obtained by Partridge, Hicks, and Smith.[4] Since that time, there have been important additional studies[10] of the system, which is shown in Figure 10-1 in a form based on the most up-to-date information. According to this information, there are only three compositions corresponding to crystalline compounds. These are the pyrophosphate (2 $Na_2O \cdot P_2O_5$), the tripolyphosphate (5 $Na_2O \cdot 3$ P_2O_5), and the metaphosphate ($Na_2O \cdot P_2O_5$) compositions. As can be seen from Figure 10-1, the pentasodium tripolyphosphate melts incongruently; that is to say, at its melting point of 622°C., $Na_5P_3O_{10}$ converts into a liquid of the composition 61.6% P_2O_5 by weight (54.9% of the total P) plus crystalline $Na_4P_2O_7$ (45.1% of the total P).

The eutectic at a temperature of 552°C. appears at a P_2O_5 content of 64.3% ,which is approximately half way between the compositions corresponding to $Na_9P_7O_{22}$ and $Na_{10}P_8O_{25}$. The material which crystallizes out at the eutectic is an intimate mixture of 45% $Na_5P_3O_{10}$-I plus 55% Na_3-P_3O_9 (this latter salt is also known as $NaPO_3$-I[4]).

At each of the three compositions where crystals are found, there are several different crystalline forms. These forms and the transitions between them are shown in Table 10-1, where it should be noted that there are from two to five crystalline forms of $Na_4P_2O_7$, two crystalline forms of $Na_5P_3O_{10}$, and six crystalline forms corresponding to the sodium metaphosphate composition.

The transitions between the various forms proposed for $Na_4P_2O_7$ are very rapid, and the only form which has been obtained at room temperature is the one which is stable at this temperature. On the other hand, the high-temperature form of $Na_5P_3O_{10}$ can readily be cooled to room temperature. In fact, this high-temperature form, $Na_5P_3O_{10}$-I, will not reconvert to the low-temperature form, $Na_5P_3O_{10}$-II, even when held for extended lengths of time at temperatures in the stability range of the latter form unless there is some amorphous material present. This matter is discussed more fully in a later section dealing with the preparation of $Na_5P_3O_{10}$.

The conversions between different crystalline forms at the metaphosphate composition are extremely complicated, as outlined in Table 10-1. Since the metaphosphate composition corresponds to ring structures and is also the limiting case for long straight chains, as well as for certain types of ultraphosphate structures (see Chapt. 11), we have the rather unusual

[10] G. W. Morey and E. Ingerson, *Am. J. Sci.*, **242**, 1 (1944); E. Ingerson and G. W. Morey, *Am. Mineralogist*, **28**, 448 (1943); and R. W. Liddell, *J. Am. Chem. Soc.*, **71**, 207 (1949).

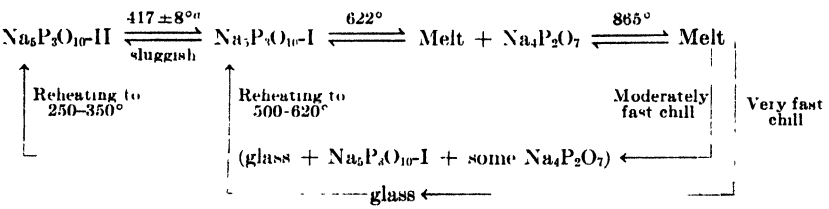
TABLE 10-1
Known Thermal Transitions in the System: Na_2O–P_2O_5[a]
(All temperatures in degrees Centigrade)

Pyrophosphates:

$$Na_4P_2O_7\text{-III} \overset{410° \pm 10°}{\rightleftharpoons} Na_4P_2O_7\text{-II} \overset{520° \pm 10°}{\rightleftharpoons} Na_4P_2O_7\text{-I} \overset{985°}{\rightleftharpoons} \text{Melt}$$

Note: All transitions are rapid and only Form III has been obtained at room temperatures.[a] Form III called V and II called III by Partridge, Hicks, and Smith.

Tripolyphosphates[10,18]



Note: Mixtures of Forms I and II can easily be brought to room temperature.[a] Either form can also be obtained pure with more difficulty. Form I will not revert to form II unless amorphous material is present Solutions of both forms are identical several hours after dissolution

[a] Thermodynamic transition temperatures are shown over the double arrows denoting reversible reactions The temperatures given for the single arrows correspond to reasonably rapid transition rates and have no connection with thermodynamic equilibria

case where the structure of the lowest temperature forms (Maddrell's salts, $NaPO_3$-II and -III) are believed to be extremely long chains, the intermediate forms are trimetaphosphate rings, and what appears to be the highest temperature form (Kurrol's salt) is a long straight chain. The ring structures are discussed in more detail in Chapter 11, and the long chains are covered toward the end of the present chapter.

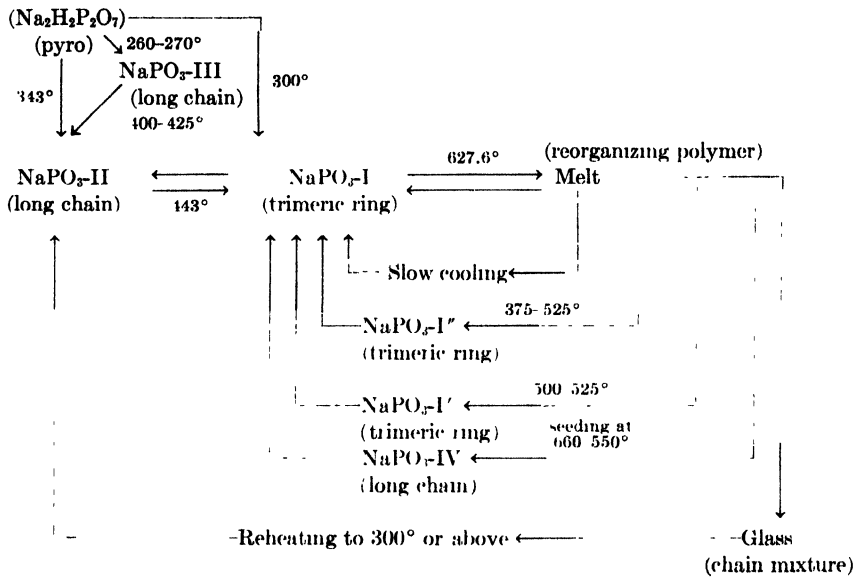
The phase diagram[11] for the potassium phosphates in the range between 2 $K_2O \cdot P_2O_5$ and $K_2O \cdot P_2O_5$ is very similar to the sodium system, as can be seen from Figure 10-2. In this case, however, there seems[12] to be only a single equilibrium crystalline form corresponding to each of the anhydrous salts $K_4P_2O_7$, $K_5P_3O_{10}$, and KPO_3, although there is far from sufficient information on the subject to make this conclusion unequivocal.

[11] G. W. Morey, *J. Am. Chem. Soc.*, **76**, 4724 (1954).

[12] R. K. Osterheld and L. F. Audrieth, *J. Phys. Chem.*, **56**, 38 (1952); A. Boullé and M. Dominé-Bergès, *International Union Pure Applied Chemistry, Colloquium of Section for Inorganic Chemistry, Munster, 2–6 Sept. 1954*, Verlag Chemie, Weinheim, Germany, 1955, pp. 253

TABLE 10-1 (*continued*)

Metaphosphates:



Note: All forms can be readily brought to room temperature. Forms I, I′, and I″ all contain the trimetaphosphate ring and easily dissolve to give supposedly identical solutions. Form IV, known as sodium Kurrol's Salt, rapidly dissolves in cold salt solutions containing cations other than sodium to give a highly viscous solution. Form III dissolves like Form IV in such salt solutions upon warming and Form II in such salt solutions upon boiling, both III and II also give viscous solutions.

These compounds will all be described later in this chapter. The eutectic in the 2 $K_2O \cdot P_2O_5$–$K_2O \cdot P_2O_5$ system appears at a temperature of 613°C., and the compound $K_5P_3O_{10}$ melts incongruently at 641.5°C.

Recent investigations by Morey and coworkers[13] have defined the Na_2O–K_2O–P_2O_5 system within the limits 2 $Na_2O \cdot P_2O_5$, $Na_2O \cdot P_2O_5$, 2 $K_2O \cdot P_2O_5$, and $K_2O \cdot P_2O_5$. In Figure 10-3, the phase diagram between $Na_2O \cdot P_2O_5$ and $K_2O \cdot P_2O_5$ is given.[11] In this phase diagram there is found a mixed crystalline metaphosphate, 3 $NaPO_3 \cdot KPO_3$, exhibiting an incongruent melting point of 552°C. This compound is a trimetaphosphate,[14] $Na_2K_3(P_3O_9)_4$, which will be discussed in greater detail in Chapter

[13] G. W. Morey, F. R. Boyd, J. L. England, and W. T. Chen., *J. Am. Chem. Soc.*, **77**, 5003 (1955); also see refs. 10, 11, and 12.

[14] E. J. Griffith and J. R. Van Wazer, *J. Am. Chem. Soc.*, **77**, 4222 (1955).

12. The eutectic in the sodium-potassium metaphosphate system comes at 547°C. and corresponds to the mole composition: 26.6% Na_2O, 23.4% K_2O, and 50.0% P_2O_5.

The binary system 2 $Na_2O \cdot P_2O_5$–2 $K_2O_5 \cdot P_2O_5$ shows a complete series of solid solutions between the sodium and potassium pyrophosphates. There

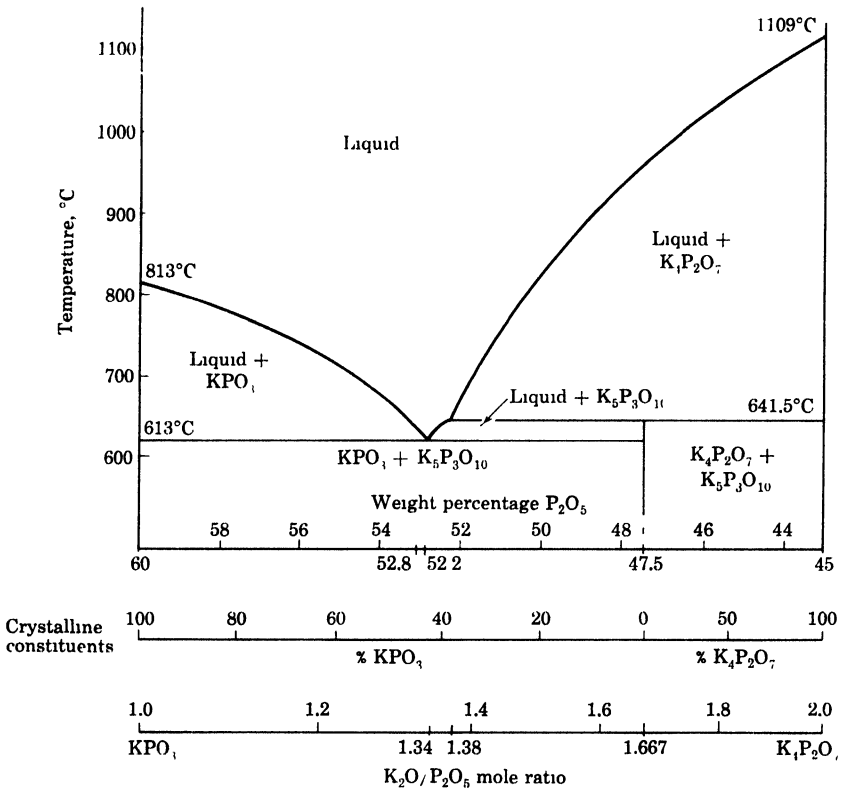


Fig. 10-2. The potassium phosphate phase diagram between $K_2O \cdot P_2O_5$ and $2K_2O \cdot P_2O_5$.

is a minimum melting point in this series of solid solutions at about 890°C., which occurs at the $Na_4P_2O_7/K_4P_2O_7$ mole ratio of about 2. In the system 5 $Na_2O \cdot 3\ P_2O_5$–5 $K_2O \cdot 3\ P_2O_5$, all of the intermediate compositions melt incongruently as do the two end members of the series, $Na_5P_3O_{10}$ and $K_5P_3O_{10}$. There is extensive solid solution in this tripolyphosphate system, and the available data indicate that there may possibly be an intermediate compound of the composition $Na_5K_5(P_3O_{10})_2$.

A projection of the entire sodium phosphate–potassium phosphate phase diagram between the points 2 $Na_2O \cdot P_2O_5$, $Na_2O \cdot P_2O_5$, 2 $K_2O \cdot P_2O_5$, and $K_2O \cdot P_2O_5$ is shown in Figure 10-4. A three-dimensional model of this same diagram is given in Figure 10-5. The lowest eutectic, *E*, shown in

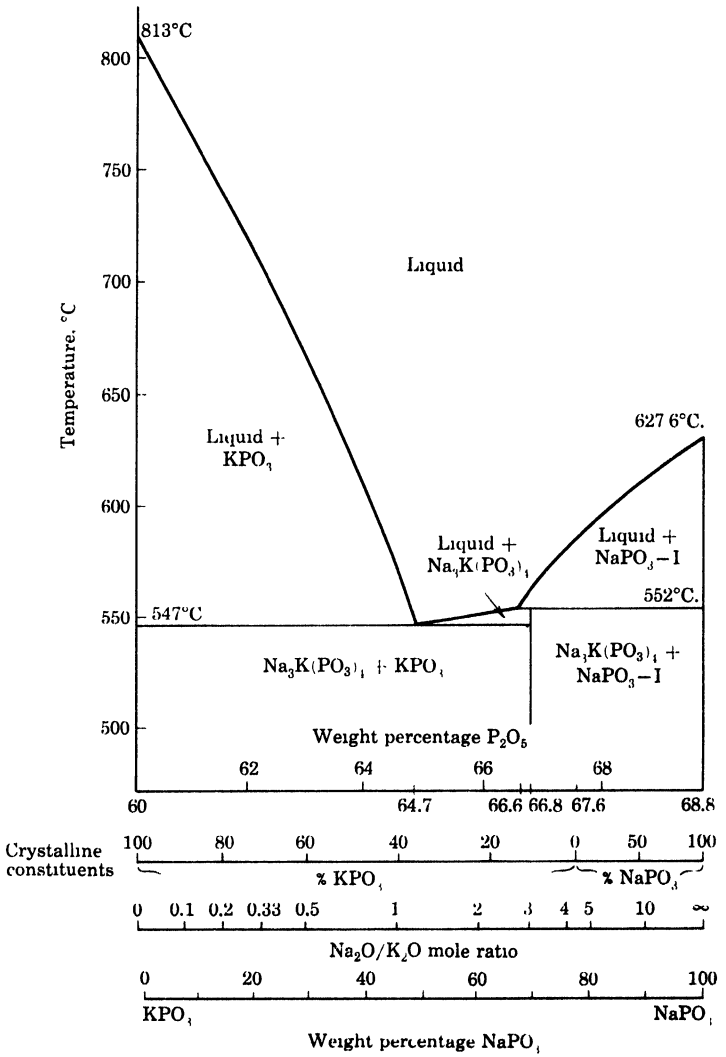


Fig 10-3. The sodium potassium metaphosphate phase diagram between $Na_2O \cdot P_2O$ and $K_2O \cdot P_2O_5$.

Figure 10-4 occurs at a temperature of 512°C. It should be noticed that the liquidus temperature in this entire diagram ranges from 512–1104°C., with the melting temperatures of the two end-member pyrophosphates being the higher points in the diagram and the eutectics at the metaphosphate end of the diagram being the lower melting compositions.

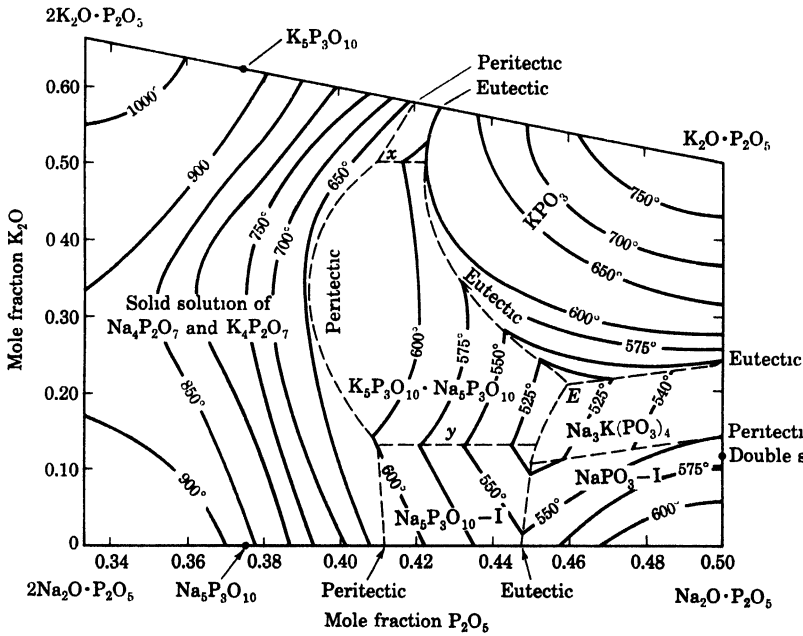


Fig. 10-4. Base plane of the Na_2O–K_2O–P_2O_5 system between $Na_2O \cdot P_2O_5$, $2Na_2O \cdot P_2O_5$, $K_2O \cdot P_2O_5$, and $2K_2O \cdot P_2O_5$. Liquidus temperatures are represented by the solid contour lines. Peritectics and eutectics are shown as dotted lines with the ternary eutectic in the system labeled *E*. The double salt shown on the right of the figure is $Na_9K_3(P_3O_9)_4$. Lines *x* and *y* are eutectics between the pure tripolyphosphates and their double salt, $Na_5P_3O_{10} \cdot K_5P_3O_{10}$, solid solution.

It is interesting to compare the sodium metaphosphate–potassium metaphosphate phase diagram of Figure 10-3 with the sodium metaphosphate–calcium metaphosphate phase diagram[15] given in Figure 10-6. The double salt in the latter system has the empirical formula $Na_4Ca(PO_3)_3$. It is not yet known whether this salt is a ring or chain compound. It should be noted that the mixed metaphosphate in the $Na_2O \cdot P_2O_5$–$CaO \cdot P_2O_5$

[15] G. W. Morey, *J. Am. Chem. Soc.*, **74**, 5783 (1952)

system does not melt incongruently but exhibits a regular melting point at 738°C.

The part of the CaO–P_2O_5 phase diagram[16] between 2 $CaO \cdot P_2O_5$ and $CaO \cdot P_2O_5$ is given in Figure 10-7. As can be seen from the figure, this

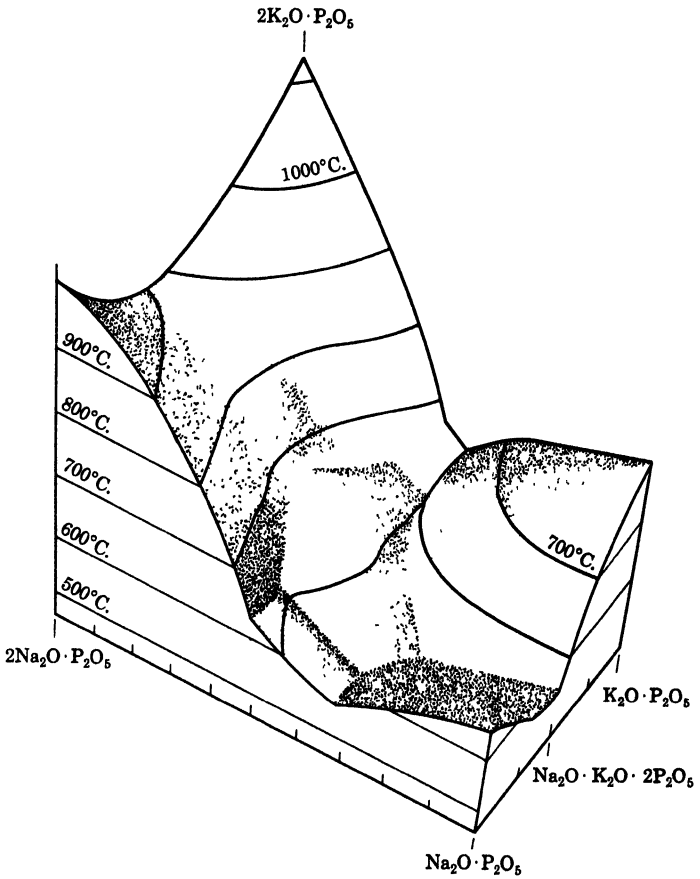


Fig. 10-5. Liquidus temperatures in the Na_2O–K_2O–P_2O_5 system between $Na_2O \cdot P_2O_5$, $2Na_2O \cdot P_2O_5$, $K_2O \cdot P_2O_5$, and $2K_2O \cdot P_2O_5$.

system shows large areas of solid solution. In addition to the two forms of the calcium metaphosphate and the two forms of the pyrophosphate, there is a third crystalline substance, trömelite. Since the x-ray pattern

[16] W. L. Hill, G. T. Faust, and D. S. Reynolds, *Am. J. Sci.*, **242**, 457, 542 (1944).

of trömelite corresponds to a considerable region of solid solutions, it is very difficult to set up a chemical formula for this substance. However, the center of its equilibrium area in the phase diagram lies near a CaO/P_2O_5 mole ratio of 1.40, which corresponds to the Berzelius formula of 7 CaO·-

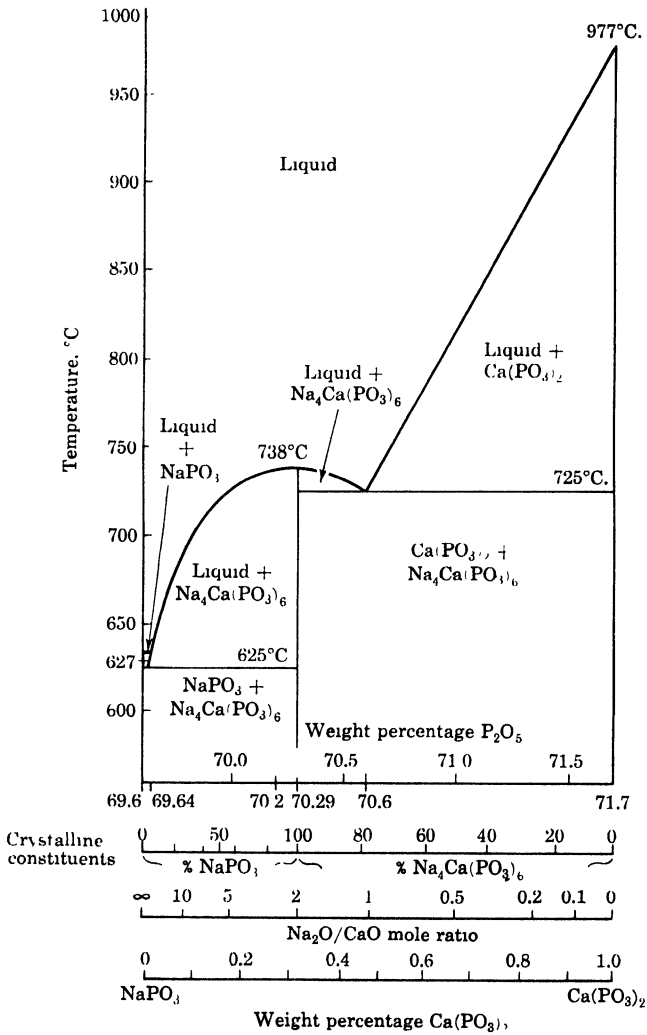


Fig. 10-6 The sodium-calcium metaphosphate phase diagram between $Na_2O \cdot P_2O_5$ and $CaO \cdot P_2O_5$

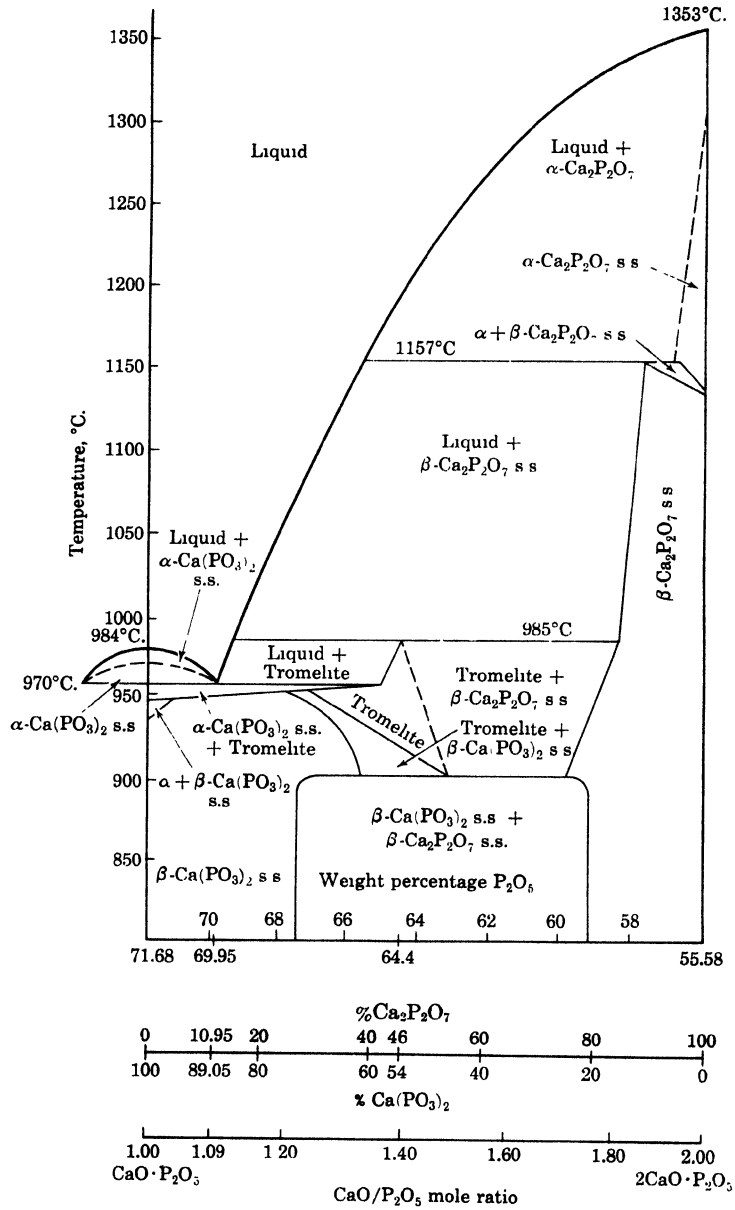


Fig. 10-7. The calcium phosphate phase diagram between $CaO \cdot P_2O_5$ and $2CaO \cdot P_2O_5$. (The s.s stand for solid solutions which are labeled with a formula of fixed stoichiometry.)

5 P_2O_5, which can be rewritten as a pentapolyphosphate, $Ca_7(P_5O_{16})_2$. Recent paper chromatographic studies[16a] have shown that trömelite is indeed a pentapolyphosphate.

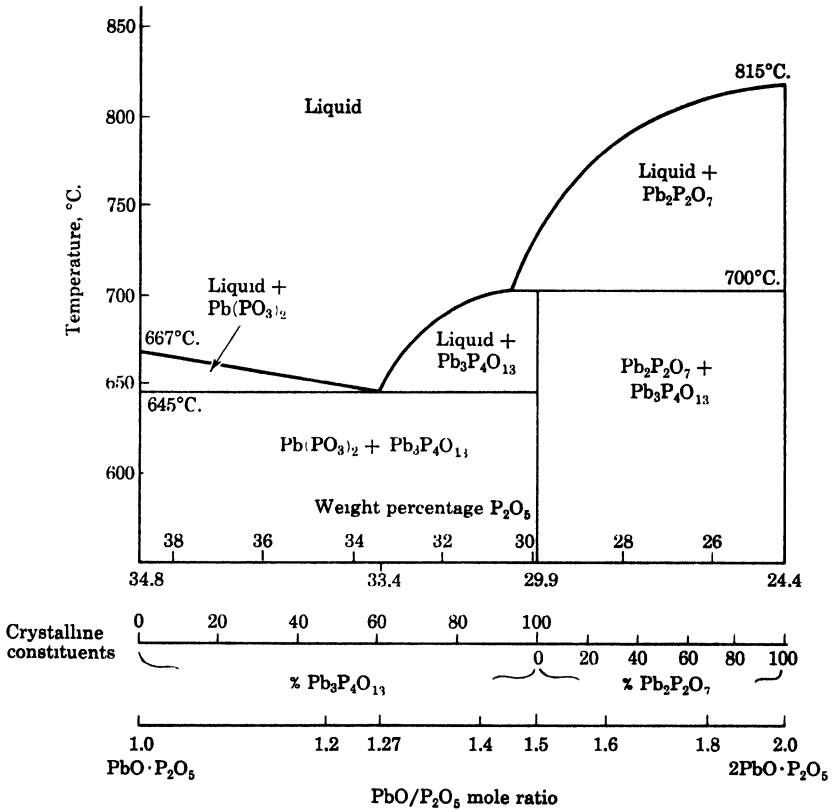


Fig 10-8 The lead phosphate phase diagram between $PbO \cdot P_2O_5$ and $2PbO \cdot P_2O_5$.

The system $2\,PbO \cdot P_2O_5$–$PbO \cdot P_2O_5$, shown in Figure 10-8,[7] is extremely interesting in that the only intermediate polyphosphate composition found in the diagram is the tetrapolyphosphate, $Pb_3P_4O_{13}$. The structure of this lead salt has been proven by paper chromatography of the sodium salt prepared from it. The metaphosphate in the lead system turns out to be a tetrametaphosphate. Other investigators[17] indicate that there is

[16a] J. R. Van Wazer and S. Ohashi, *J. Am. Chem. Soc.*, **80**, 1010 (1958).

[17] F. Warschauer, *Z. anorg. Chem.*, **36**, 137 (1903). R. K. Iler, *J. Phys Chem.*, **56**, 1086 (1952).

also a long chain lead metaphosphate which, when solubilized by reacting with a solution of sodium sulfide, gives a viscous sodium phosphate. In

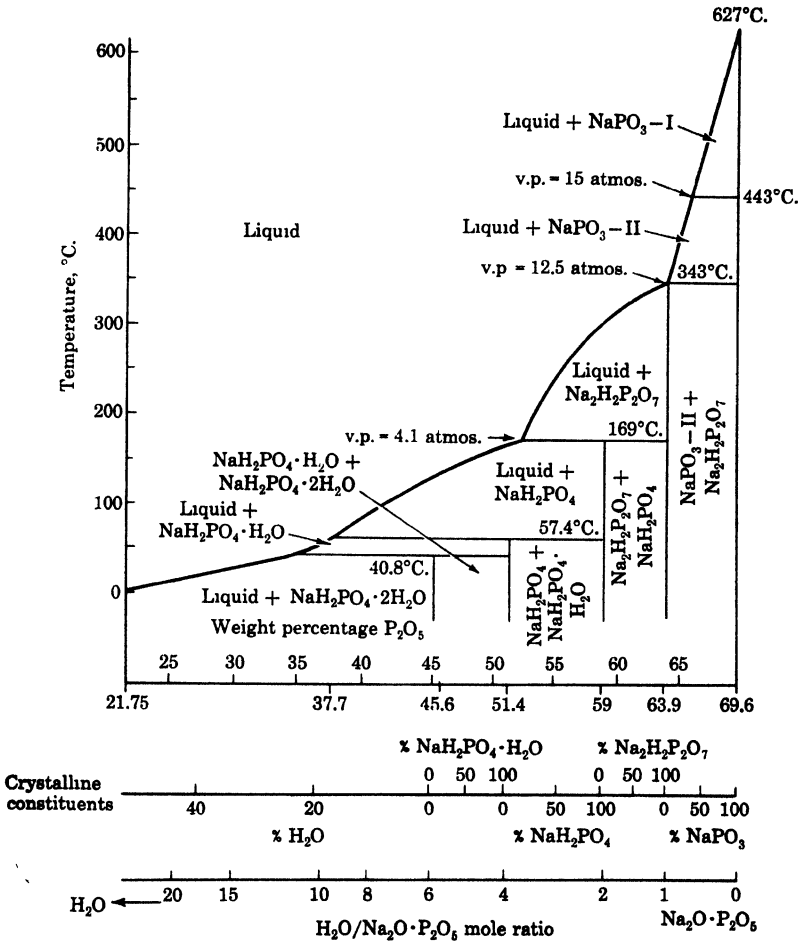


Fig. 10-9. Phase diagram of the H_2O–$Na_2O \cdot P_2O_5$ system.

its freedom from solid solution, the 2 $PbO \cdot P_2O_5$–$PbO \cdot P_2O_5$ system is similar to the respective sodium and potassium systems.

Only a small cross section of the system Na_2O–H_2O–P_2O_5 has been determined; and this is the section in which Na_2O/P_2O_5 is kept at unity,

and the H_2O content is varied, starting at 0% H_2O. The phase diagram[18] corresponding to this section is shown in Figure 10-9, where it should be noticed that in addition to the sodium metaphosphates, both disodium pyrophosphate and monosodium orthophosphate are in equilibrium with

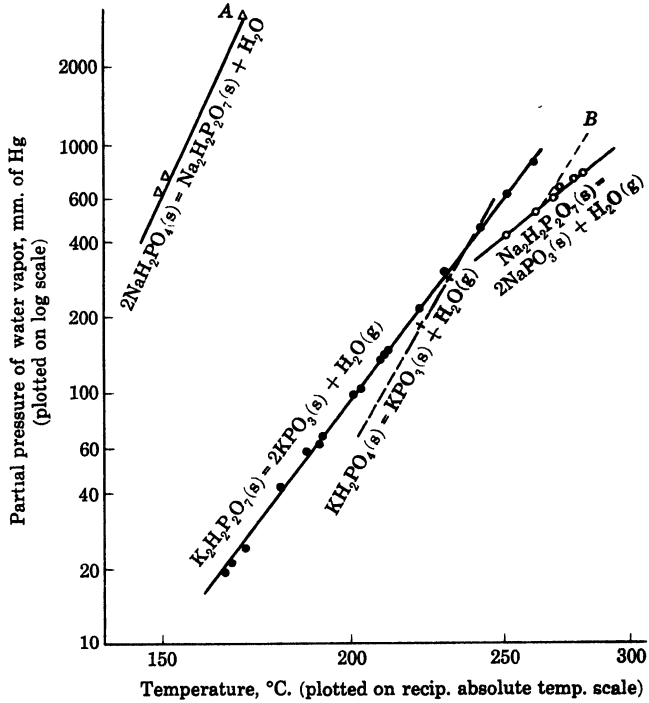


Fig. 10-10. Equilibrium constants (partial pressure of water vapor) for phosphate condensation reactions. Regions in which equilibrium was reached from both sides and the phosphates were solids are given by solid lines. Point *A* is from Figure 10-9, and line *B* is an extrapolation toward another point taken from Figure 10-9.

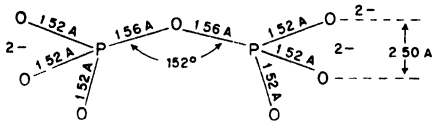
the liquid phase. This phase diagram is different than the other ones presented here, in that the others were obtained at constant pressure, while this one corresponds to widely varying pressures of water vapor. It is instructive to compare the equilibrium data of Figure 10-9 with those of Figure 10-10, where the dissociation pressure of water vapor over a mixture of $Na_2H_2P_2O_7$ and $NaPO_3$ is presented as a function of temperature.

[18] G. W. Morey, *J. Am. Chem. Soc.*, **75**, 5794 (1953); also private communications.

PYROPHOSPHATES

History and Structure of the Pyrophosphate Anion

Although the present-day formulation of pyrophosphoric acid as two PO_4 groups joined together by the sharing of a common oxygen atom appeared in the chemical literature during the first half of the 19th century, other possible formulations[19] involving "pentavalent" phosphorus could also be found through the first quarter of the 19th century. The presently accepted structure of the pyrophosphate anion is given below, along with the dimensions obtained by x-ray:



(10-1)

The main proof for this structure is an x-ray study[20] of the isomorphic pyrophosphates of silicon, titanium, zirconium, tin, hafnium, and uranium. All of these compounds exhibit cubic crystals with four molecules per unit cell. In the ZrP_2O_7 compound, the dimensions of the $P_2O_7^{4-}$ ion were found to be those given in structure 10-1. In addition, a whole host of physical measurements on solutions of the pyrophosphates are in agreement with this structure. Thus, the limiting electrical conductivity is found to correspond to a 4− ionic charge (see Fig. 8-8) while the Raman spectra[21] and nuclear magnetic resonance[22] of the phosphorus atom in this compound are in accord with the symmetry of structure 10-1.

Thermal Preparation of Crystalline Alkali Metal Pyrophosphates and Pyrophosphoric Acid

The two common sodium salts of pyrophosphoric acid are tetrasodium pyrophosphate, $Na_4P_2O_7$, and disodium pyrophosphate, $Na_2H_2P_2O_7$—

[19] For example, D. Balareff, *Z. anorg. u. allgem. Chem.*, **118**, 123 (1921); also see J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green & Co., London, 1928, Vol. VIII, p. 971.

[20] G. R. Levi and G. Peyronel, *Z. Krist.*, **92**, 190 (1935); G. Peyronel, *ibid.*, **94**, 311 (1936).

[21] T. J. Hanwick and P. O. Hoffmann, *J. Chem. Phys.*, **17**, 1166 (1949); **19**, 708 (1951).

[22] J. R. Van Wazer, C. F. Callis, and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 4945 (1955); J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956); C. F. Callis, J. R. Van Wazer, J N. Shoolery, and W. A. Anderson, *ibid.*, **79**, 2719 (1957).

both of which have been known for over a century. These two salts can be prepared in anhydrous form by thermal dehydration of orthophosphates, according to the following over-all equations

$$2\,Na_2HPO_4(s) \longrightarrow Na_4P_2O_7(s) + H_2O(g) \qquad (10\text{-}2)$$

$$2\,NaH_2PO_4(s) \longrightarrow Na_2H_2P_2O_7(s) + H_2O(g) \qquad (10\text{-}3)$$

Investigation of these two dehydration processes shows that they are relatively simple and straightforward, as compared to the thermal dehydration of orthophosphates to make pentasodium tripolyphosphate—a process which is described later in this chapter. In the dehydration of Na_2HPO_4, as usually carried out, there appears to be no intermediate amorphous phase. As the Na_2HPO_4 disappears, $Na_4P_2O_7$ builds up to take its place. This process, however, can be speeded up[23] by adding a small amount of a more acidic salt, such as NaH_2PO_4 or $NaHSO_4$ to the Na_2HPO_4. In this case, the formation of a plastic, amorphous phase accelerates the growth of crystals of $Na_4P_2O_7$.

The conversion of NaH_2PO_4 to $Na_2H_2P_2O_7$ also seems to be straightforward under ordinary conditions, in that there is, again, no intermediate amorphous form. As shown in Figure 10-9, the stable phase at temperatures in the range from 169–375°C. is $Na_2H_2P_2O_7$ in the system where Na_2O/P_2O_5 equals unity, and there are varying amounts of H_2O. As indicated by this information, disodium pyrophosphate is usually made by heating to final temperatures near 200°C. At temperatures of about 250°C. and above, the $Na_2H_2P_2O_7$ further converts at reasonably rapid rates to the various sodium metaphosphates. This conversion of $Na_2H_2P_2O_7$ to ring or long chain structures is a major problem in the thermal preparation of $Na_2H_2P_2O_7$. It will be discussed under sodium trimetaphosphate in Chapter 11.

A study of the equilibrium pressure of water vapor over a mixture of ortho- and pyrophosphates and pyro- and metaphosphates has been made for both the sodium and potassium systems.[24] The data from this work, shown in Figure 10-10, are believed to be reasonably sound, as the equilibrium was approached from both sides in the temperature range for which experimental points are given. As can be seen from the slope of the lines in Figure 10-10, the heat of the reaction whereby monosodium orthophosphate converts into sodium acid pyrophosphate plus water vapor is 14 kcal./mole of phosphorus at temperatures near 150°C., as compared to 6 kcal./mole of phosphorus at temperatures near 250°C.

[23] J. W. Edwards, U. S. patent application of the Monsanto Chemical Co.

[24] S. J. Kiehl and G. H. Wallace, *J. Am. Chem. Soc.*, **49**, 376 (1927).

for the further conversion of the sodium acid pyrophosphate to an unspecified sodium metaphosphate plus water vapor. If the average value of the points obtained by Kiehl and Wallace for the conversion of sodium acid pyrophosphate to a metaphosphate is connected to the pressure measured for this conversion by Morey, the slope of the connecting line corresponds to about 11 kcal./mole of phosphorus. This latter value corresponds reasonably well with the calorimetrically measured heats of formation for $Na_2H_2P_2O_7$ and $NaPO_3$ (probably the trimetaphosphate, $NaPO_3$-II) from which a heat of reaction of 14 kcal./mole of phosphorus is calculated.

Pyrophosphoric acid crystallizes slowly from the syrupy liquids in the H_2O–P_2O_5 system for which the H_2O/P_2O_5 mole ratio is near two. The crystalline acid always contains some ortho- and longer chain phosphates. The crystalline acid is readily prepared by adjusting the water in a condensed phosphoric acid so that the H_2O/P_2O_5 mole ratio equals 2.00 and then allowing the acid to stand for about a month. Adjustment of the H_2O/P_2O_5 ratio has been carried out commercially by evaporation of water from an orthophosphoric acid; but best results in the laboratory are achieved by adding the proper amount of phosphorus pentoxide to 85% H_3PO_4, with some heating to effect dissolution.

Physical Properties of Crystalline Sodium Pyrophosphates and Pyrophosphoric Acid

Pyrophosphoric acid, $H_4P_2O_7$, in the crystalline state melts at 61°C. to give a reorganizing liquid containing, at equilibrium, 17.2% orthophosphoric acid, 42.5% pyrophosphoric acid, 25.0% tripolyphosphoric acid, and 10.5% of tetrapolyphosphoric acid, with the remainder being higher chain phosphoric acids (see p. 753). Crystalline pyrophosphoric acid is very hygroscopic and will dissolve in the moisture picked up on prolonged exposure to the atmosphere. There is a simple eutectic[25] between the crystalline ortho- and pyrophosphoric acids. This eutectic occurs at 62 wt.-% $H_4P_2O_7$ in the H_3PO_4–$H_4P_2O_7$ mixture (*i.e.*, at 76.0 wt.-% P_2O_5) and at a temperature of 16°C.

When pure solutions of pyrophosphoric acid are needed for study, it is better to prepare them from the sodium salt, $Na_4P_2O_7$, by using cation exchange resins, than to dissolve the crystalline acid. However, the crystalline acid is a useful reagent for preparing relatively unstable pyrophosphates, such as the ammonium salt, in concentrated form. The dissocia-

[5] C. L. Ward and J. L. Cross, unpublished data of the Monsanto Chemical Co.

tion constants[26] of pure pyrophosphoric acid in dilute aqueous solution at 25°C. have the following values: $K_1 \approx 10^{-1}$, $K_2 \approx 10^{-2}$, $K_3 = 2.7 \times 10^{-7}$, and $K_4 = 2.4 \times 10^{-10}$.

Unfortunately, only a part of the solubility curve in the system NaOH–$H_4P_2O_7$–H_2O has been determined to date.[27] This is given in Figure 10-11. These data show another reason, in addition to the fact that they can be readily prepared by thermal methods, why the tetrasodium and disodium

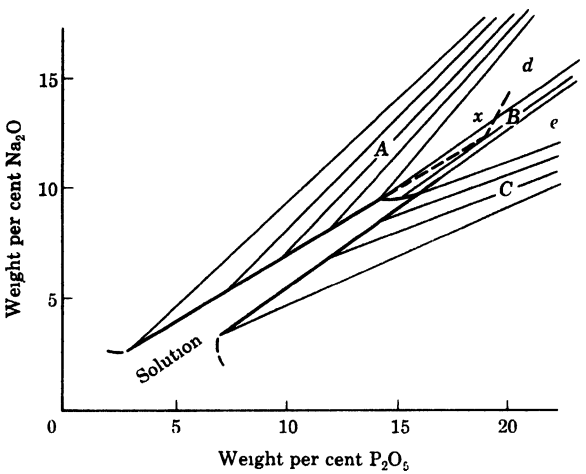


Fig. 10-11. The system Na_2O–P_2O_5–H_2O for the sodium pyrophosphates at 20°C. at 1 atmosphere. Region *A* represents a two-phase area of $Na_4P_2O_7 \cdot 10H_2O$ plus solution; region *B*, a two-phase area of $Na_3HP_2O_7 \cdot 9H_2O$ plus solution, and region *C*, a two-phase area of $Na_2H_2P_2O_7 \cdot 6H_2O$ plus solution. Regions *d* and *e* are three-phase areas. The solubility curve of $Na_4P_2O_7 \cdot 10H_2O$ can extend into a metastable region as denoted by the dotted line marked *x*.

salts are so well known as compared to the intermediate trisodium salt, $Na_3HP_2O_7$. In the solubility diagram of Figure 10-11, it is seen that the trisodium salt, as the nonahydrate, exists in equilibrium with a saturated solution only in a small range of solution composition; and, indeed, it often does not crystallize at all because of the metastability of its neighboring salts, the solubility curves of which are shown in the metastable region as dotted lines. Because of slow hydrolytic degradation, the solu-

[26] C. B. Monk, *J. Chem. Soc.*, **1949**, 423; I. M. Kolthoff and W. Beach, *Rec. trav chim.*, **47**, 826 (1928); G. A. Abbott and W. C. Bray, *J. Am. Chem. Soc.*, **51**, 763 (1909)

[27] L. Selva (1935) in A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds*, 3rd ed., D. Van Nostrand & Co., New York, 1940, Vol. I, pp. 1292–93

bility curve of Figure 10-11 and all other systems of water plus condensed phosphates under normal conditions represent thermodynamically metastable systems—the truly stable systems would consist of the orthophosphate degradation products.

The solubilities[28] of anhydrous tetrasodium pyrophosphate and its only hydrate—a decahydrate—are shown in Figure 10-12. As can be seen from this figure, the invariant point at which the anhydrous salt and the decahydrate are in equilibrium with their solution is 79.5°C. The

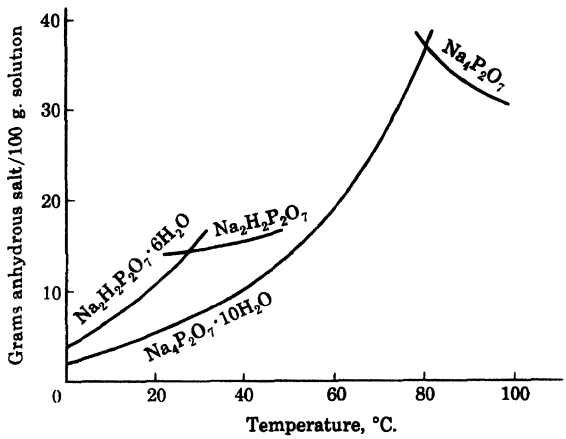


Fig. 10-12. Solubilities of sodium acid pyrophosphate and tetrasodium pyrophosphate as a function of temperature

partial pressure of water vapor over a mixture of the hydrate and anhydrous salts, $Na_4P_2O_7 \cdot 10\ H_2O + Na_4P_2O_7$, is 12.5 mm. of Hg at 25°C. and 113 mm. at 60°C. The temperature variation of this partial pressure ($\log p \sim 1/T$) is in agreement with the calorimetrically measured heat of hydration of 23.5 kcal./mole of salt. The calorimetric measurements give +11.65 kcal./mole for the heat of solution[29] of $Na_4P_2O_7$ in 800 moles of water and −11.7 kcal./mole for the heat of solution[29,30] of the $Na_4P_2O_7 \cdot 10\ H_2O$ in water. It is interesting to note that pressure-temperature curves have been reported[31] for solutions of $Na_4P_2O_7$ and $K_4P_2O_7$ at tem-

[28] H. Menzel and L. Sieg, *Z. Elektrochem.*, **38**, 283 (1932).

[29] J. Thomsen, *Thermochem. Untersuch.* (*Leipzig*), **3**, 118 (1883)

[30] H. Giran, *Compt. rend.*, **134**, 1499 (1902).

[31] G. W. Morey and W. T. Chen, *J. Am. Chem. Soc.*, **78**, 4249 (1956).

peratures in the range of 375–1100°C. Unfortunately, the amount of hydrolysis to orthophosphate was not determined in this work.

The solubility of the disodium salt, $Na_2H_2P_2O_7$, is also shown in Figure 10-12. This salt appears as a hexahydrate as well as the anhydrous material.[32] As can be seen from Figure 10-12, the transition temperature between the hydrate and anhydrous forms in the presence of their saturated solution is 27°C

In addition to the tetrasodium and disodium salts described above, the less common trisodium pyrophosphate[33,34] can be obtained as either the

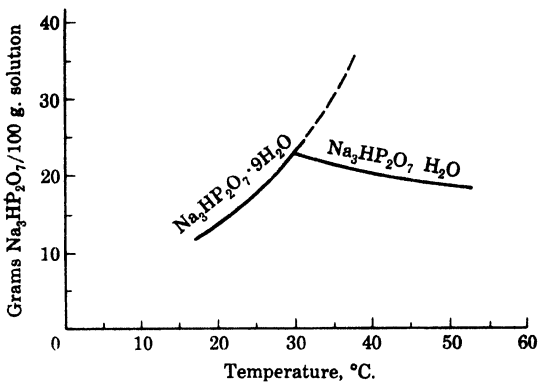


Fig. 10-13 Solubility of trisodium pyrophosphate in percentage of anhydrous salt plotted as a function of temperature.

anhydrous form, $Na_3HP_2O_7$; the monohydrate, $Na_3HP_2O_7 \cdot H_2O$; or the nonahydrate, $Na_3HP_2O_7 \cdot 9\ H_2O$. Solubility data[33] for the monohydrate are given in Figure 10-13. Several hydrates of $Na_3HP_2O_7$ intermediate between the mono- and nonahydrate have been reported[35] in the literature These, however, are mixtures of the mono- and nonahydrate which are obtained because the nonahydrate effloresces readily. The anhydrous salt is made by heating the monohydrate for several days at 150°C.

A monosodium pyrophosphate is also known.[34,35] This is obtained by

[32] The hexahydrate was first described by K. J. Bayer, *J. prakt. Chem.*, **106**, 501 (1869). A tetrahydrate was also discussed by C. F. Rammelsberg, *Chem. Abhandl. Berlin*, **1888**, 127; however, the hexahydrate is the only hydrate which is recognized today.

[33] F. E. Hubbard, *Ind. Eng. Chem.*, **41**, 2908 (1949).

[34] J. R. Partington and H. E. Wallsom, *Chem. News*, **136**, 97 (1928); T Saltzer, *Arch. Pharm.*, **232**, 365 (1894); also see ref. 29.

[35] G V Susich and H. Friedrich, *P B Report* 73552 (Fr. 5571-6) (about 1946).

reacting $Na_2H_2P_2O_7$ with $H_4P_2O_7$ and separating the $NaH_3P_2O_7$ from excess pyrophosphoric acid by repeatedly pressing it between clay plates and finally washing with absolutely anhydrous ether. This material exhibits a unique x-ray pattern[28] and converts in the presence of water or methanol to $Na_2H_2P_2O_7$ and $H_4P_2O_7$. It is said that, when $NaH_3P_2O_7$ is added to water it can be recrystallized by evaporation; but addition of alcohol to a concentrated solution precipitates the disodium salt. Monosodium pyrophosphate is very soluble in water. A solubility of 63 g. $NaH_3P_2O_7$/100 ml. of saturated solution has been reported.[36]

Other Alkali Metal Pyrophosphates

The salt $K_4P_2O_7$ is well known. It was first prepared by Graham[37] by the usual procedure of dehydrating K_2HPO_4. At temperatures near 250°C., the K_2HPO_4 begins to dehydrate, with the process becoming rapid at about 350°C.[12,38] Material held at 400°C. and above is pure $K_4P_2O_7$. Unlike the case of the sodium system, it is difficult to form $K_2H_2P_2O_7$ by heating KH_2PO_4, since the rate of decomposition of the $K_2H_2P_2O_7$ to $(KPO_3)_n$ is about as rapid as the rate of its formation under most conditions.[38,39] However, some $K_2H_2P_2O_7$ can be made by thermal dehydration of KH_2PO_4 in a moist atmosphere.[40] Equilibrium measurements[24] of the partial pressure of water corresponding to the following equations show that, at elevated temperatures, the potassium acid pyrophosphate is thermodynamically unstable to either potassium Kurrol's salt, KPO_3, or monopotassium orthophosphate. This is graphically illustrated by Figure 10-10, from which the following heats of reaction were calculated:

$$K_2H_2P_2O_7(s) \xrightarrow{\Delta} 2\,KPO_3(s) + H_2O(g),\ \Delta H = 7.3 \text{ kcal./mole of P} \quad (10\text{-}4)$$

$$KH_2PO_4(s) \xrightarrow{\Delta} KPO_3(s) + H_2O(g),\ \Delta H = 23 \text{ kcal./mole of P} \quad (10\text{-}5)$$

Since the monopotassium orthophosphate melts at about 250°C. during its dehydration to potassium Kurrol's salt and measured partial pressures[24]

[36] H. Giran, *Ann. chim. et phys.*, **30**, 249 (1903).

[37] T. Graham, *Phil. Trans.*, **123**, 253 (1833); *Ann. Physik*, **32**, 33 (1834).

[38] H. N. Terem and S. Akalan, *Compt. rend.*, **228**, 1374 (1949).

[39] L. Hackspill and R. Lauffenburger, *Compt. rend.*, **193**, 397 (1931); A. Boullé, *Ann. Chim.*, **17**, 213 (1942) and others. Also see E. Thilo and H. Grunze, *Z. anorg. u. allgem. Chem.*, **281**, 262 (1955); R. K. Osterheld and M. M. Markowitz, *J. Phys. Chem.*, **60**, 863 (1956).

[40] C. R. McCullough, U. S. Pat. 2,021,102 (1932, assigned to Monsanto Chem. Co.)

of water over this melt are lower than the extrapolated equilibrium partial pressures over a $K_2H_2P_2O_7$–KPO_3 crystal mixture at the same temperatures, there is not much chance of thermally obtaining crystalline $K_2H_2P_2O_7$ except as an unstable intermediate, the formation of which has a relatively low free energy of activation under certain favorable experimental conditions (see the formation of $Na_5P_3O_{10}$-I at temperatures where it is unstable, pp. 645–646).

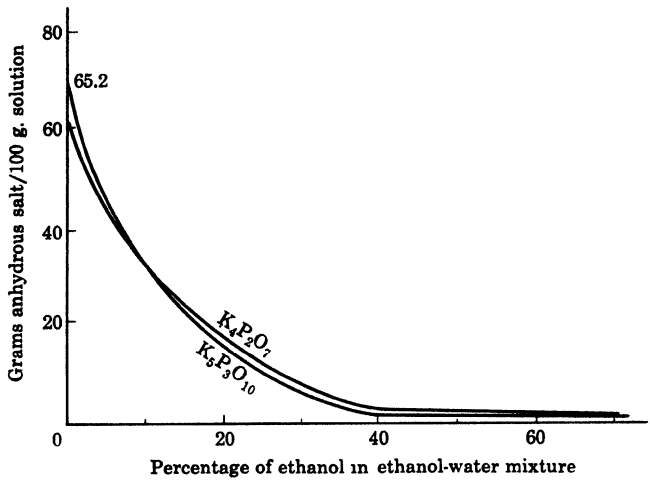


Fig. 10-14. Solubility of potassium pyrophosphate and of potassium tripolyphosphate in ethanol-water mixtures at 25°C

The usual method of making $K_2H_2P_2O_7$ is by crystallizing it from an acidified aqueous solution of $K_4P_2O_7$. Thus, a good yield of the acid pyrophosphate is obtained by adding HCl to a solution of $K_4P_2O_7$ so as to lower the pH to 4.5 and then causing precipitation by addition of alcohol.

A study[41] has been made of the KCl–$K_4P_2O_7$ system in which a eutectic was found at 735°C. corresponding to 15% $K_4P_2O_7$. This system shows no evidence of double salt or intermediate compound formation.

The solubility of tetrapotassium pyrophosphate in water is very high, and the presence of small amounts of the orthophosphate (such as may be found in some commercial preparations) increases the solubility. At 25°C., the solubility[42] is 187.4 g. of $K_4P_2O_7$/100 g. of H_2O. At 50°C., the

[41] M. Amadori, *Atti accad. nazl. Lincei, Mem. Classe sci. fis. mat. e nat., Sez. II*, **21**, 182 (1912).

[42] C. B. Durgin and R. N. Foster, data from the files of the Monsanto Chemical Co.

solubility increases to about 205 and at 75°C. to about 240 g./100 g. H_2O. The integral heat of solution of $K_4P_2O_7$ in 75 moles of water is 13 kcal./mole. The solid in equilibrium with the saturated solution is a trihydrate, $K_4P_2O_7 \cdot 3H_2O$. This hydrate, which has been known for many years,[43] is most easily prepared by adding alcohol to a concentrated solution of $K_4P_2O_7$ at room temperature. There is also a monohydrate.[42] The partial pressure of water vapor over the monohydrate is about 5 mm. of Hg

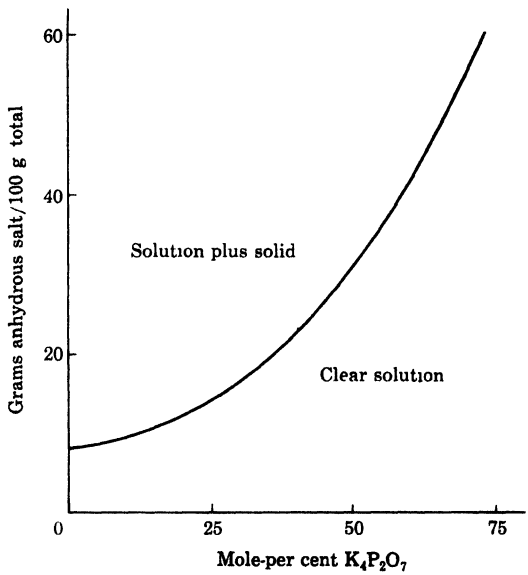


Fig. 10-15 Solubility limit of solutions of mixed sodium-potassium pyrophosphates at 30°C.

and over the trihydrate is about 10 mm. of Hg at 25°C. Thus, the anhydrous salt and its monohydrate are very hygroscopic, whereas the trihydrate will pick up water when the relative humidity is above about 45%.

The solubility[44] of tetrapotassium pyrophosphate in water-ethanol mixtures is presented in Figure 10-14. As demonstrated by this figure, the solubility is very low (<1.5 g./100 g. soln.) at concentrations of ethanol greater than about 40%, but there is a rapid rise in the amount of dissolved $K_4P_2O_7$ as the ethanol concentration is reduced from 40% to zero.

[43] A. Schwarzenberg, *Ann.*, **65**, 133 (1848).

[44] P. G. Arvan, R. P. Langguth, R. L. Rebertus, and R. R. Eckstein, technical information of the Monsanto Chemical Co.

The acid salt, $K_2H_2P_2O_7$ forms a monohydrate when crystallized from water at room temperature. This salt is very soluble in water and can be dehydrated[24] to the anhydrous salt by heating at 155°C.

The solubility limit[44] in the $K_4P_2O_7$–$Na_4P_2O_7$ system at 30°C. is presented in Figure 10-15, where it can be seen that there is a gradual increase in solubility when going from the pure sodium toward the potassium salt. When these solutions of mixed sodium-potassium pyrophosphates are caused to crystallize, the sodium salt comes out first, since the potassium phosphates are so much more soluble than the sodium salts. However, by rapidly drying the solution (as on a drum drier) a mixed salt can be obtained. X-ray powder patterns of the $Na_4P_2O_7 \cdot K_4P_2O_7$, 1:1 salt completely precipitated from aqueous solution by rapid addition of methanol were found to be nearly identical to those of the respective $Na_4P_2O_7$–$K_4P_2O_7$ solid solutions made by thermal dehydration of the mixed orthophosphates.

A mixed sodium ammonium pyrophosphate can be prepared by ammoniating solutions of $Na_2H_2P_2O_7$. This crystalline salt, $Na_2(NH_4)_2P_2O_7 \cdot 6\ H_2O$, is soluble to the extent of 33 g. of the hexahydrate per 100 g. of solution.[44] The pH of its 1% solution is 8.7.

Tetrammonium pyrophosphate can be made by either an ion exchange procedure or by ammoniating an ice-cold solution of crystalline pyrophosphoric acid.[44] An anhydrous crystalline salt, $(NH_4)_4P_2O_7$, is obtained by precipitation with ethanol. The partial pressure of ammonia over the nonacidic ammonium phosphates, such as either $(NH_4)_4P_2O_7$ or $Na_2(NH_4)_2P_2O_7$, is relatively high, so that these salts tend to lose ammonia when allowed to stand in open containers.

The substituted ammonium salts of pyrophosphoric acid can be similarly prepared. Thus, tetradiethanolamine pyrophosphate, $[(HOCH_2CH_2)_2NH_2]_4P_2O_7$, has been made[44] as a very viscous liquid which is miscible with water and with ethanol-water mixtures containing less than 40% ethanol but is only soluble to the extent of about 15 g./100 g. of solution in a 75% ethanol-25% water mixture at 25°C.[44]

Alkali Metal Pyrophosphate Peroxidates

Several of the pyrophosphate salts can be solvated with hydrogen peroxide instead of water.[45] Of these, probably the best known is the well-crystallized salt, $Na_4P_2O_7 \cdot 3\ H_2O_2$. This salt is easily prepared by grad-

[45] H. Menzel and C. Gäbler, *Z. anorg. u. allgem. Chem.*, **177**, 187 (1928); S. Husain and J. R. Partington, *Trans. Faraday Soc.*, **24**, 235 (1928); also see G. R. Levi and F. Battaglino, *Gazz. chim. ital.*, **67**, 659 (1937).

ually adding 90% H_2O_2 to powdered anhydrous $Na_4P_2O_7$ which is being continuously blended at room temperature. The salt can also be crystallized from a peroxide solution. When this salt is dissolved in water, it acts exactly like an equivalent mechanical mixture of hydrogen peroxide and tetrasodium pyrophosphate, giving the reactions typical of each and not acting like a perphosphate.

In addition to $Na_4P_2O_7 \cdot 3\ H_2O_2$, several other pyrophosphates have been prepared with peroxide of crystallization. These are $K_4P_2O_7 \cdot 3\ H_2O_2$ and $(NH_4)_2H_2P_2O_7 \cdot H_2O_2 \cdot 2\ H_2O$. Mixed H_2O–H_2O_2 derivatives of $Na_4P_2O_7$ have been described; these may be mixtures of separate crystals of hydrates and peroxidates.

Thermally Prepared Pyrophosphates of Other Metals

A very large number of pyrophosphate compositions have been prepared by thermal dehydration of the disubstituted orthophosphates of various metals. It is generally assumed that these materials are true pyrophosphates having the $P_2O_7^{4-}$ anion, but there is really no sound reason for this assumption, since it is conceivable that a substance of this composition might be a mixture of, say, ortho- and tripolyphosphates. In general, the normal pyrophosphates of multiply charged or heavy metal ions are extremely insoluble in water.

Two normal pyrophosphates of calcium are known,[16] α- and β-$Ca_2P_2O_7$. They are shown in the phase diagram of Figure 10-7.

One of the most interesting of the pyrophosphates of multiply charged metal ions is silicon pyrophosphate. The double oxide formulation of this crystalline compound is $SiO_2 \cdot P_2O_5$, which—with lack of additional information—can be written as a number of different compounds, such as silicon pyrophosphate, SiP_2O_7, siliconyl metaphosphate, $SiO(PO_3)_2$, or perhaps a three-dimensional mixed oxide. Since this substance cannot be dissolved in any solvent without decomposition, the only solution to its structure lies in an analysis by x-ray diffraction. This analysis has been carried out[20] and shows the structure to be SiP_2O_7, since the silicon atom is surrounded by six oxygen atoms (a common cationic coordination), and the P_2O_7 arrangement of two PO_4 groups connected together by the sharing of an oxygen atom was found. This is the only oxygen-containing compound of silicon having an oxidation number of +4 in which the silicon exhibits a coordination number other than four. This six-fold coodination of silicon in SiP_2O_7 shows that the phosphorus atom is more strongly bonded to oxygen when it is in the sp^3-hybrid state than is silicon in the

same state. In addition to the cubic form of SiP_2O_7, on which the structure study was made, there is also an anisotropic crystal form.[46]

Zirconium pyrophosphate, which is similar to silicon pyrophosphate, has been studied over a wide range of temperatures.[47] This compound exhibits a transition between a high- and a low-temperature form at 300°C., with both forms having a primitive cubic cell. At the transition temperature, the cell constant of the high-temperature form is $a_0 = 9.28$ A. and of the low form is $a_0 = 8.271$ A. At temperatures greater than 1500°C., ZrP_2O_7 loses P_2O_5 rather readily to form the composition $2\ ZrO_2 \cdot P_2O_5$, which has been formulated as a zirconyl pyrophosphate, $(ZrO)_2P_2O_7$. This latter compound will withstand temperatures of 1600°C. without appreciable volatilization of P_2O_5. Below 600°C., it has a very low reversible thermal expansion, which rises sharply at higher temperatures.

Precipitated Pyrophosphates of Various Metals

A large number of precipitated pyrophosphates made by combining soluble salts of multiply charged or heavy metals with tetrasodium pyrophosphate in solution were described in 1848.[43,48] As a rule, the products analyzed by these early workers had been dried at 100°C., so that many of the hydrates which were mentioned in this early literature are doubtful. The more recent literature[49] gives considerably more details about the methods of preparation, but these articles involve considerable discussion of hypothetical structures of the double salts.

Generally speaking, when equivalent amounts of soluble metal salts and $Na_4P_2O_7$ solutions are mixed, a predominantly amorphous precipitate forms which persists for long periods of time without becoming crystalline The majority of these freshly formed precipitates are easily soluble in acids. Schwarzenberg[48] and later authors have dissolved these precipitates in

[46] See A. Boullé and R. Jary, *Compt. rend.*, **237**, 161, 328 (1953); *International Union Pure Applied Chemistry, Colloquium of Section for Inorganic Chemistry. Munster, 2–6, Sept. 1954*, Verlag Chemie, Weinheim, Germany, 1954, p. 224.

[47] D. E. Harrison, H. A. McKinstry, and F. A. Hummel, *J. Am. Ceramic Soc.*, **37**, 277 (1954).

[48] H. Beer, *Ann. Physik*, **75**, 152 (1848); T. Persos, *Ann. chim. et phys.*, **20**, 315 (1847); *Ann.*, **65**, 163 (1848); T. Fleitmann and W. Henneberg, *Ann.*, **65**, 387 (1848).

[49] H. Bassett, W. L. Bedwell, and J. B. Hutchinson, *J. Chem. Soc.*, **1936**, 1412; A. Rosenheim *et al.*, *Ber.*, **48**, 582 (1915); *Z. anorg. u. allgem. Chem.*, **153**, 126 (1926); P. Pahl Ofvers, *Kgl. Vet. Akad. Forh.*, **30**, 29 (1873); *Bull. soc. chim. France*, **19**, 115 (1873); also see *Ber.*, **6**, 1465 (1873) and *ibid.*, **7**, 478 (1874). There are also many scattered references in the literature to such pyrophosphates.

sulfurous acid in order to grow reasonably large crystals by slow removal of the SO_2 to give homogeneous precipitation of the pyrophosphate. Other acids have also been used for this purpose. Crystalline pyrophosphates have been prepared by starting with the acidic salt, $Na_2H_2P_2O_7$, plus the soluble salt of the multiply charged metal ion and raising the pH slowly so that microscopic crystals will form. In addition, an excess of $Na_4P_2O_7$ can be employed in order to solubilize the salts by complexing action. In such cases, crystalline precipitates often can also be obtained. In the case of the precipitates of magnesium and nickel and a few other pyrophosphates, the solubility is high enough in pure water so that crystalline salts are formed by simply digesting the amorphous precipitates for a long time. Such salts are sufficiently soluble so that crystalline products can even be derived from mixtures containing an excess of the soluble salt of the multiply charged metal ion.

A few crystalline pyrophosphates obtained by precipitation from solutions of the alkali metal pyrophosphates are listed in Table 10-2 These salts are listed as examples of the various types of precipitated crystalline pyrophosphates. The first two examples in the table are illustrative of the kind of solid solutions sometimes observed. The variety of hydrates of $Mg_2P_2O_7$ show how many different hydrated species may exist for a given salt The chromium and manganese pyrophosphates demonstrate considerable change in color with change in composition, and the ferric salts show how, even in the presence of a large amount of water of hydration, the iron does not exhibit the customary brown color of the ferric ion. The copper compound, $Na_6Cu(P_2O_7)_2 \cdot 16\ H_2O$, is very different from most double salts of the pyrophosphates which are only slightly soluble in water $Na_6Cu(P_2O_7)_2 \cdot 16\ H_2O$ dissolves congruently to form a saturated solution containing 37 g. of $Na_6Cu(P_2O_7)_2$ per 100 g. of solution at 25°C. Due to its high solubility, this salt can be produced as large crystals which are prismatic in shape and have a dark blue color as compared to similarly sized pale blue (nearly white) crystals of the other cupric pyrophosphates.

Because of its high solubility, it appears that the structure units in $Na_6Cu(P_2O_7)_2 \cdot 16\ H_2O$ are not bound together very firmly. Presumably the deep coloration shows that the copper ion is strongly coordinated either by water [as in $Cu(OH_2)_4^{2+}$] or, more probably, by the pyrophosphate ions [as in $Cu(P_2O_7)_2^{2-}$]. In most of these pyrophosphates, the multiply charged or heavy metal ion serves to tie the whole structure together, and the bonds between it and the phosphate part of the structure seem to exhibit considerable covalent character. This accounts for the low solubilities and the colors which are often very different from that of

TABLE 10-2
Some Precipitated Pyrophosphates

Salt	Remarks	Authors[a]
$Mg_2P_2O_7 \cdot 6\ H_2O$ $Na_2Mg_2(P_2O_7)_2 \cdot 10\ H_2O$	Solid solution with Na-salt as limiting case	B
$Mg_2P_2O_7 \cdot 6.25\ H_2O$ $Na_{28}Mg_{20}(P_2O_7)_{22} \cdot 172\ H_2O$	Solid solution	B
$Mg_2P_2O_7 \cdot 2\ 67\ H_2O$		
$Mg_2P_2O_7 \cdot 3.67\ H_2O$		
$Mg_2P_2O_7 \cdot 4\ H_2O$		
$Mg_2P_2O_7 \cdot 5\ H_2O$		
$Mg_2P_2O_7 \cdot 6\ 5\ H_2O$		
$Mg_2P_2O_7 \cdot 7\ H_2O$		
$NaCrP_2O_7 \cdot 8\ H_2O$	Grey-blue color	R
$NaCrP_2O_7 \cdot 5\ H_2O$	Green	
$KCrP_2O_7 \cdot 5\ H_2O$	Bright green	
$(NH_4)CrP_2O_7 \cdot 6\ H_2O$	Grey-blue	
$NaMnP_2O_7 \cdot 5\ H_2O$	Bluish red color	R
$KMnP_2O_7 \cdot 5\ H_2O$	Violet	
$KMnP_2O_7 \cdot 3\ H_2O$	Red	
$AgMnP_2O_7 \cdot 3\ H_2O$	Violet	
$BaMnP_2O_7 \cdot 3\ H_2O$	Rose	
$Na_6Fe_2(P_2O_7)_3 \cdot 9\ H_2O$	Grey-white color	R
$Na_8Fe_4(P_2O_7)_5 \cdot 28\ H_2O$	White with tan cast	
$Na_6Cu(P_2O_7)_2 \cdot 16\ H_2O$	Dark blue; very soluble	B
$Na_{32}Cu_{14}(P_2O_7)_{13} \cdot 13\ H_2O$	Light blue; insoluble	
$Na_4Cu_3(P_2O_7)_2 \cdot 17\ H_2O$	Light blue; insoluble	

[a] B = Bassett, Bedwell, and Hutchinson, ref. 49. R = Rosenheim and Triantaphyllides, ref. 49

the given metal ion in aqueous solutions of its simple salts and in hydrates of its salts with essentially noncomplexing anions such as NO_3^- or SO_4^{2-}.

Hydrolysis of the coacervate formed by treating vitreous calcium metaphosphate with water leads to the formation of two crystalline calcium pyrophosphates.[49a] One of these compounds (which may exhibit a region of crystalline solid solution) has the formula $Ca_3H_2(P_2O_7)_2 \cdot 4H_2O$, and the formula of the other is $Ca_2P_2O_7 \cdot 2H_2O$.

Soluble Pyrophosphato Complexes

Because it has been accepted as a chemical entity for over a hundred years, the pyrophosphate ion has received somewhat more scientific study

[49a] E. H. Brown, J. R. Lehr, J. P. Smith, W. E. Brown, and A. W. Frazier, *J. Phys. Chem.*, **61**, 1669 (1957).

TABLE 10-3
Pyrophosphate Complexes of Various Metals

Metal complexed	Total conc. metal ion moles/l (range)	Moles P_2/ Moles M	Other conditions[a]	Average pK$_D$ reported by investigator[b]	Method	Remarks
K	0 12	0 50	t = 25	0 80	pH titration	
Na	0 12	0 50	t = 25	1 00	pH titration	
Na	4.6×10^{-4} to 20×10^{-4}	0 50	t = 25	2 35	Electrical conductivity	Debye-Huckel limiting theoretical activity coefficients applied
Ca	$3\ 92 \times 10^{-4}$	36	t = 25 pH = 8 0	–	Solubility $CaHPO_4$	
Ca	ca 9×10^{-6}	$>10^3$	$\mu \approx 0\ 15$ pH = 7 4 t = 37	3 46	Ion exchange equilibria	
Cu	$2\text{–}3 \times 10^{-4}$	<4	t = 25	6 40	Polarograph	Equilibrium is $Cu(HP_2O_7)^- \rightleftharpoons Cu^{2+} + HP_2O_7^{3-}$
	$2\text{–}3 \times 10^{-4}$	>4	pH = 3 5–5 $\mu \approx 0\ 6$	10 0	Polarograph	Equilibrium is $Cu(HP_2O_7)_2^{4-} \rightleftharpoons Cu^{2+} + 2HP_2O_7^{3-}$
Cu	2×10^{-3} to 20×10^{-3}	10 to 20	t = 25 pH 7-10 μ = 1	8 80	Solubility of copper ferrocyanide	
Cu	5×10^{-4} to 200×10^{-4}	Continuous variation used	t = 25 μ = 1 pH = 7–10	12 57	Spectrophotometric	Equilibrium is $Cu(P_2O_7)_2^{6-} \rightleftharpoons Cu^{2+} + 2\ P_2O_7^{4-}$

[a] μ is the ionic strength and t is the temperature in °C.

[b] Negative logarithm equilibrium dissociation constant for the 1:1 metal-to-phosphate complex in which all ionizable hydrogens are removed from the phosphate molecule (unless otherwise designated under Remarks)

as a complexing agent than have the other polyphosphates or mixtures of polyphosphates.[50] The dissociation constants of the pyrophosphate complexes of sodium, calcium, and copper are shown in Table 10-3. In spite of the fact that the pyrophosphate ion is a strong complexing agent, it is not used much in commercial applications for sequestering agents, since precipitates of the pyrophosphates of multiply charged metal ions are extremely insoluble and this insolubility tends to counteract the complexing ability of the pyrophosphate ion

Pyrophosphate Esters

A number of esters of pyrophosphoric acid are known Of these the tetraethyl pyrophosphate is particularly important because of its action as an insecticide. This substance has been carefully prepared[51] by the controlled hydrolysis of diethyl chlorophosphate using pyridine as the alkali to absorb the HCl given off according to the following equation:

$$2\,(C_2H_5O)_2P(O)Cl + HOH \longrightarrow (C_2H_5O)_2P(O)OP(O)(C_2H_5)_2 + 2\,HCl \quad (10\text{-}6)$$

In commercial production, a great deal of this material has been made in impure form by reacting ethanol with phosphorus pentoxide Tetraethyl pyrophosphate in impure form is a liquid which boils at 104 110°C[52] at 0.08 mm. pressure Its index of refraction is 1.4170 for the sodium-D line at 25°C. and its density, d^{25}, is 1.1845 Evolution of ethylene is observed when tetraethyl pyrophosphate is heated at temperatures above 208°C.

The tetraalkyl pyrophosphates hydrolyze to dialkyl orthophosphates by scission of the P—O—P linkage of the pyrophosphate. The rate of this hydrolysis has been measured[52] without pH control in dilute solution so that, in the case of tetraethyl pyrophosphate, the pH dropped from an original value of 3.2 to a final value of 2.0–2.1 during hydrolysis. Under these conditions, a rate constant of 0.10 $hr.^{-1}$ was obtained at 25°C. as compared to a constant of 0.0016 $hr.^{-1}$ for the pyrophosphate ion at a pH of 2.5 and 25°C. in the presence of tetramethyl ammonium bromide. This means that the tetraethyl ester hydrolyzes about 60

[50] F. T. Wall and R. H. Doremus, *J. Am. Chem. Soc.*, **76**, 868 (1954); C. B. Mack, *J. Chem. Soc.*, **1949**, 423; R. E. Gosselin and E. R. Coghlan, *Archiv Biochem. Biophys.*, **45**, 301 (1953); J. I. Watters and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **15**, 8 (1943); *ibid.*, **16**, 187 (1944); *J. Am. Chem. Soc.*, **70**, 2455 (1948); J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).

[51] A. D. F. Toy, *J. Am. Chem. Soc.*, **70**, 3882 (1948). Also see F. H. Brock, *J. Org. Chem.*, **22**, 1114 (1957).

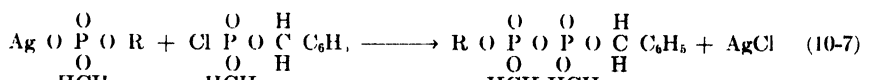
[52] S. A. Hall and M. Jacobson, *Ind. Eng. Chem.*, **40**, 694 (1948).

times faster than the $H_2P_2O_7^{2-}$ ion Even though the pH was not controlled, the over-all rate process for hydrolysis of the ester appeared to be first order; and the activation energy was found to be about 10.3 kcal./mole of P--O—P linkages as compared to the 25 kcal./mole found in hydrolysis of the P--O—P linkages in noncrosslinked condensed phosphate salts. In another study[51] the rate of hydrolysis of the tetraalkyl pyrophosphates was found to decrease as the size of the alkyl group was increased. Thus at 25°C. with uncontrolled (as well as unrecorded) pH, the rate constants were 1.5 $hr.^{-1}$ for methyl, 0.10 $hr.^{-1}$ for ethyl, and 0.04 $hr.^{-1}$ for *n*-propyl pyrophosphate.

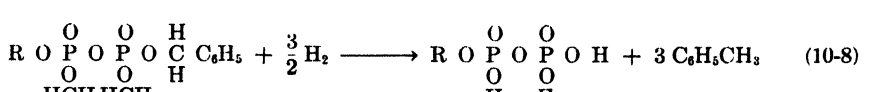
Presumably this rapid hydrolysis of the P--O--P linkage in the tetraalkyl pyrophosphates is related to the unusually rapid hydrolysis at branching points (Antibranching Rule), since in both cases the PO_4 group in question does not have a charge, and hydrolysis leads to the formation of two charged oxygen atoms which do not serve to connect the PO_4 group in question to other atoms in the molecule ion. The presence of two to four nonbridging oxygens per PO_4 group appears to stabilize the resonance in the group.

Organic Pyrophosphates of Biological Importance

A number of organic derivatives of pyrophosphate play an important role in biology Of these, adenosine-5′-diphosphate is especially noteworthy, in that the hydrolysis of the adenosine triphosphate to this compound is a source of immediate biological energy. Adenosine diphosphate has been synthesized[53] from a chlorophosphate and the silver salt of its monophosphate, with the unwanted active sites on both orthophosphates being protected by benzyl groups. This reaction in which silver chloride is formed is shown in equation 10-7 below. The protective benzyl groups are removed by hydrogenation, as illustrated in equation 10-8.



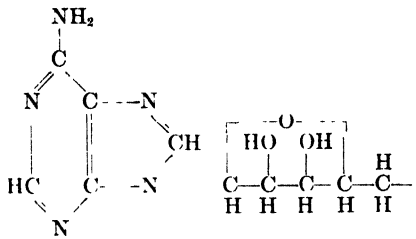
(10-7)



(10-8)

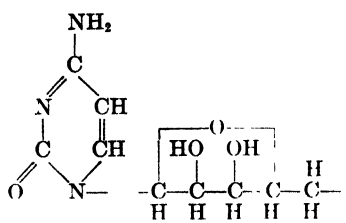
[53] A. R. Todd, *J. Chem. Soc.*, **1946**, 647; J. Baddiley and A. R. Todd, *ibid.*, **1947**, 648

where R = the adenosine radical,

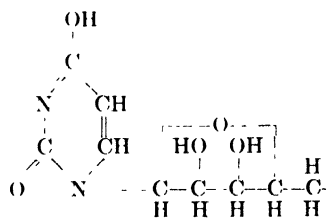


(10-9)

A number of other 5′-ribonucleotides have also been shown to play a role in biology as pyrophosphates. For these the radical R exhibits the following structures:

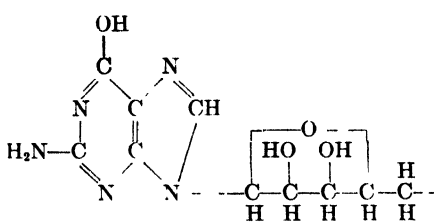


cytidine radical



uridine radical

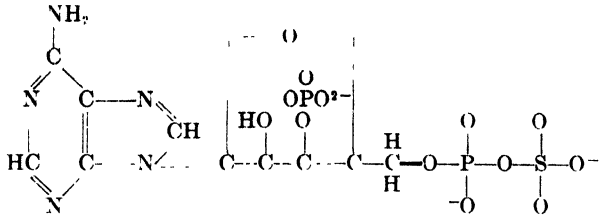
(10-10)



guanosine radical

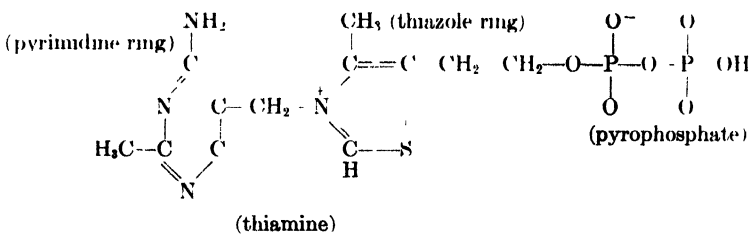
An interesting sulfate-phosphate closely related to the 5′-ribonucleotides is adenosine 3′-phosphate-5′-phosphosulfate which has the structure shown below.[54] This recently verified compound is a strong sulfate donor—reacting, for instance, with nitrophenol to give nitrophenyl sulfate in an enzymatically catalyzed equilibrium reaction

[54] P. W. Robbins and F. Lipmann, *J. Am. Chem. Soc.*, **78**, 2653 (1956). H. Hilz and F. Lipmann, *Proc. Natl. Acad. Sci.*, **41**, 880 (1955); also see J. D. Gregory and Y. Nose, *Federation Proc.*, **16**, 189 (1957).



(10-11)

Several coenzymes contain pyrophosphate groups. One of these is cocarboxylase or thiamine pyrophosphate, the structure of which is shown below.[55] This coenzyme is active in the decarboxylation of α-keto acids by carboxylase There is also a thiamine triphosphate which is believed to exhibit the structure of 10-12 except that the $-NH_2$ group on the pyrimidine ring is substituted by a OPO_3^{2-} group. The thiamine "polyphosphates" are thus pyrophosphates with orthophosphates attached to the thiamine part of the molecule-ion.[55]

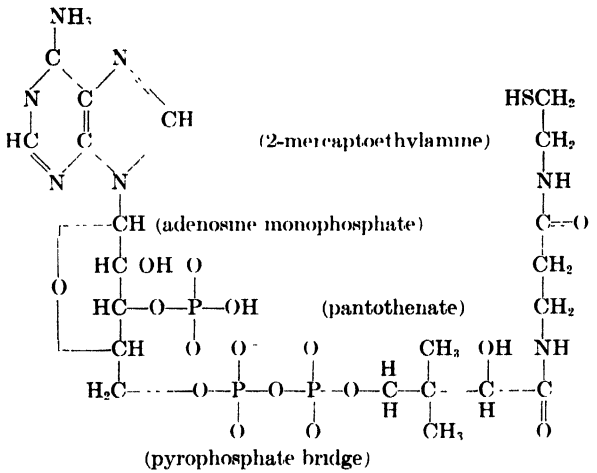


(10-12)

Another pyrophosphate which is important in biology is coenzyme A in which an adenosine monophosphate moiety is attached by means of a pyrophosphate bridge to a pantothenate moiety terminated by 2-mercaptoethylamine.[56] Coenzyme A acts with condensing enzymes by carrying an acetyl group in acetylation reactions. The probable structure is given below, although there is uncertainty about the position of the orthophosphate on the adenosine and about the point of attachment of the pyrophosphate bridge to the pantothenate portion of the coenzyme.

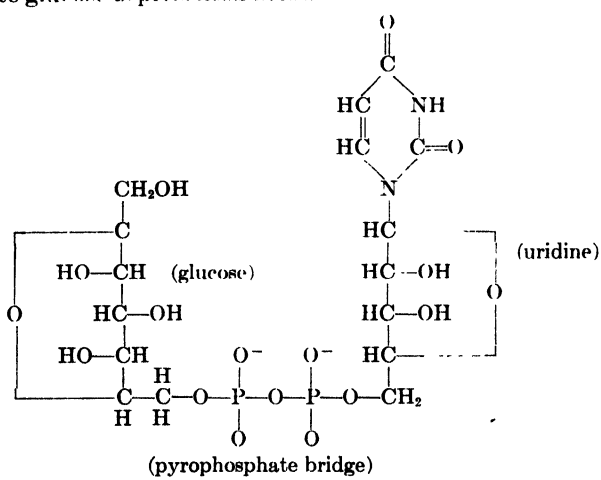
[55] J. Weyland and H. Tauber, *J. Am. Chem. Soc.*, **60**, 2263 (1938); H. Weil-Malherbe, *Biochem. J.*, **34**, 980 (1940); P. Karrer and M. Viscontini, *Helv. Chim. Acta*, **29**, 1901 (1946); also see H. Roux, Y. Feysseire, and G. Duchesne, *Bull. soc. chim. biol.*, **30**, 592 (1948).

[56] F. Lipmann, *Bact. Rev.*, **17**, 1 (1953). G. D. Novelli, *Phosphorus Metabolism*, ed. W. D. McElroy and B. Glass, Johns Hopkins Press, Baltimore, Md., 1951, Vol I, pp 414–17.



(10-13)

Uridine diphosphate glucose (UDPG) is a coenzyme for isomerases, which catalyze Walden inversions such as the conversion of galactose-1-phosphate to glucose-1-phosphate. The probable structure[57] of uridine diphosphate glucose is presented below

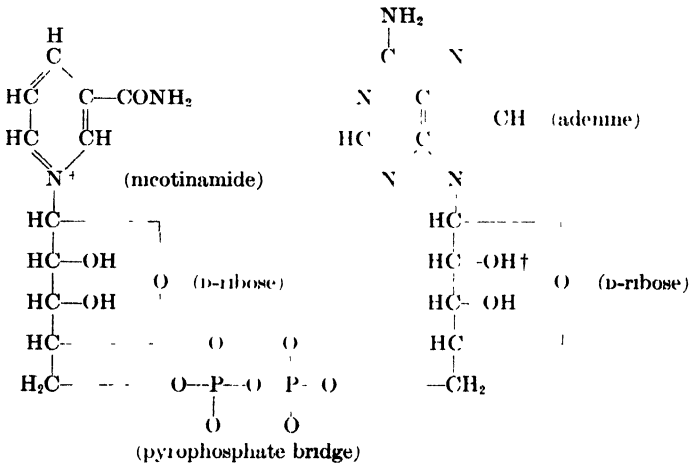


(10-14)

Both diphosphopyridine nucleotide (DPN, or coenzyme I) and triphosphate pyridine nucleotide (TPN, or coenzyme II) are structures in which two moieties are connected by means of a pyrophosphate bridge.[55] The structure given below is that of the diphosphate pyridine nucleotide.

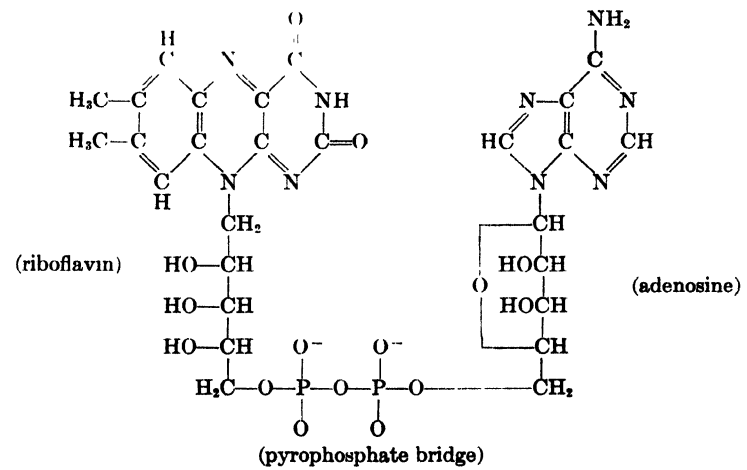
[57] R. Caputto, L. F. Leloir, C. E. Cardini, and A. C. Paladini, *J. Biol. Chem.*, **184**, 333 (1950).

The triphosphate derivative is exactly the same[58] except that the OH group at the 2′ carbon atom of the D-ribose (which is marked in the diagram with a dagger) is esterified with orthophosphoric acid. Both of these materials are coenzymes for dehydrogenases, since they play the role of hydrogen acceptors in the oxidation of organic compounds



(10-15)

Flavin adenine dinucleotide (FAD) is a coenzyme which exhibits functions similar to those of the pyridine nucleotides (DPN and TPN). The structure proposed for this compound is given below.[59]



(10-16)

[58] F. W. Allen, *Ann. Rev. Biochem.*, **10**, 221 (1941). A. Kornberg and W. E. Price Jr., *J. Biol. Chem.*, **186**, 557 (1950).

[59] O. Warburg and W. Christian, *Biochem. Z.*, **298**, 150 (1938).

In the various coenzymes listed above, the pyrophosphate merely modifies the properties of the organic part of the molecules which act directly in the respective biological reactions. Scission and formation of P—O—P linkage in the pyrophosphate part of the over-all structure or scission and formation of the C—O—P linkages connecting the pyrophosphate to the rest of the molecule are not important in the major biological functions of these compounds.

TRIPOLYPHOSPHATES

History of Sodium Tripolyphosphate

Crystalline pentasodium tripolyphosphate was first described by Schwartz[60] in 1895. This original preparation of a relatively pure crystalline sodium tripolyphosphate was made by melting together the proper ratio of tetrasodium pyrophosphate and sodium metaphosphate and allowing the melt to cool slowly. The optical properties described for the crystals obtained in 1895 compare very well with modern information. However, the existence of a sodium tripolyphosphate was questioned by a number of later authors, and it was not until a series of papers by Huber[2] and by Andress and Wüst,[3] that the salt was accepted and a real start was made in elucidating its properties. The phase study of Partridge, Hicks, and Smith[4] removed any further questions of doubt.

At the present time, two anhydrous crystalline forms are known[4,10]: the high-temperature variety, Form I, and the low-temperature variety, Form II. Since the transition between these two forms is sluggish (if such a simple word can be used to describe the complicated phenomena which are observed!), they can both be obtained as relatively pure species or as mixtures at room temperature. In addition, there is a crystalline hexahydrate,[3] $Na_5P_3O_{10} \cdot 6\ H_2O$. References in the early literature[60] to an octahydrate have not been confirmed, and the modern consensus[61] is that it does not exist.

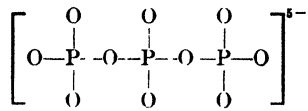
Proof of Structure of Tripolyphosphate Anion

At the present time it is quite universally accepted that the tripolyphosphate anion exhibits the following structure, drawn in the usual two-

[60] (a) F. Schwartz, *Z. anorg. Chem.*, **9**, 249 (1895); also see (b) M. Stange, *ibid.*, **12**, 444 (1898).

[61] For example, P. Bonneman and M. Bassiere, *Compt. rend.*, **204**, 433 (1937); **206**, 1379 (1938).

dimensional form used in organic chemistry except that π-bonding is omitted. Naturally, the four nearest oxygens tetrahedrally surround each phosphorus atom, and the P—O—P bond angles are approximately the same as the O—P—O bond angles.



(10-17)

This structure is not based on a complete x-ray study of the crystal, although a preliminary analysis of the x-ray data indicates that this anion is present in the two anhydrous forms[62] of $Na_5P_3O_{10}$. At the present time, symmetry data and the size of the unit cell have been obtained on Forms I and II,[62] as well as on the hexahydrate.[63] From these x-ray data, all that can be said with certainty is that there are four molecules of $Na_5P_3O_{10}$ in the unit cell of Forms I and II and two molecules in the unit cell of the hexahydrate. X-ray structure data are not reported on any other tripolyphosphate.

The structure of the sodium tripolyphosphate anion, shown in formula 10-17 above, is quite firmly based on seven pieces of information, none of which is completely unequivocal in itself. However, when these seven points are considered as a body, they supply fairly formidable evidence for the accepted structure. The seven structure proofs are listed below:

1. The composition of the salt is 5 $M_2O \cdot 3\ P_2O_5$, and it occurs as a unique crystalline entity in both the Na_2O–P_2O_5 and K_2O–P_2O_5 phase diagrams.[4,10,11,13] The simplest formula corresponding to 5 $M_2O \cdot 3\ P_2O_5$ is $M_5P_3O_{10}$, and this formula can only be fulfilled with interlinked PO_4 tetrahedra by the structure given in formula 10-17. (For a review of the various ways that PO_4 tetrahedra can be put together to form triphosphates, see Table 8-3 on page 425. It should be noticed in this table that there is only one structure which fits the formula $M_5P_3O_{10}$.)

2. pH titration shows that the ratio of weak (or end group) hydrogen ions to strong (one per phosphorus atom) hydrogen ions is 2:3. This is in accord with the accepted structure.

3. Cryoscopy[64] in sodium sulfate decahydrate shows the proper molecular weight for the monomer of $Na_5P_3O_{10}$.

[62] J. J. Dymon and A. J. King, *Acta Cryst.*, **4**, 378 (1951).

[63] P. Bonneman and M. Bassiere, *Compt. rend.*, **206**, 1379 (1938).

[64] P. Bonneman, *Compt. rend.*, **204**, 433 (1937). Bonneman's value of the molecular weight was 2% high. This value has been made even more precise; see ref. 68

4. In paper chromatography or ion exchange chromatography, the tripolyphosphate ion appears at the proper point for a three-membered chain, calculated on the basis that the orthophosphate is the monophosphate and the pyrophosphate the two-membered chain (see Fig. 10-22).

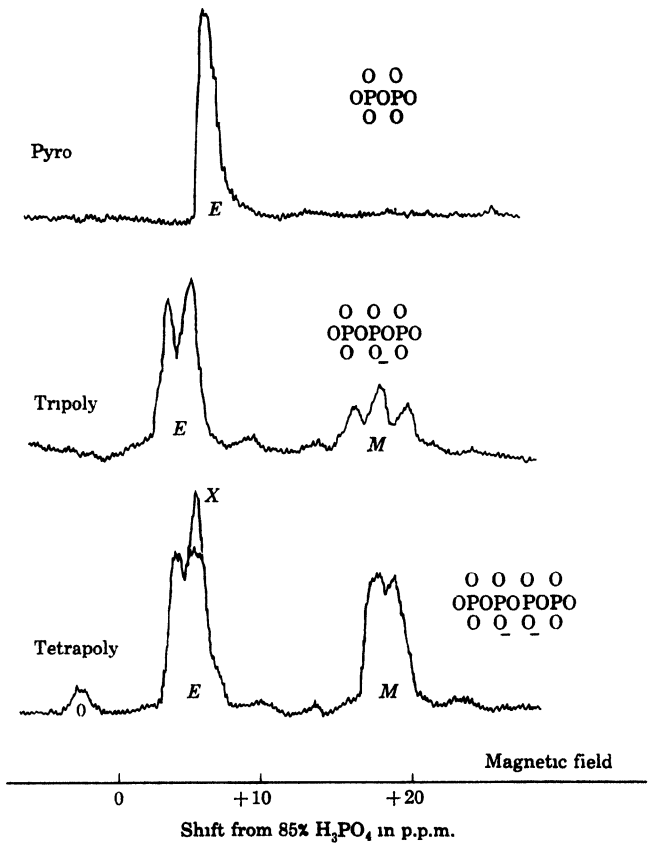


Fig. 10-16. Nuclear magnetic resonance spectra of chain-phosphate anions at 7140 gauss and 12.3 megacycles as adjusted to the same scale. The end-group peaks are denoted by *E*, and the middle-group peaks by *M*. Orthophosphate impurity is denoted by *O*, and the extra height of the peak marked *X* is due to some pyrophosphate impurity.

5. The nuclear magnetic spectrum,[22] shown in Figure 10-16, exhibits two major peaks, one of which has been shown to correspond to end groups and the other to middle groups by comparing nuclear magnetic resonance spectra[22] of a number of different phosphates. Moreover, the area under

the peaks demonstrates that the ratio of end groups to middle groups is 2:1. The end-group peak is split into a doublet because each end PO_4 group is attached to one middle group, and the middle-group peak is a triplet because each middle PO_4 group is attached to two end groups. The only structure which is in accord with these data is the one shown above as formula 10-17. This work is the most conclusive proof of the structure of the $P_3O_{10}^{5-}$ anion of $Na_5P_3O_{10}$.

6. Hydrolysis[65] of the tripolyphosphate anion has been shown to give one mole of pyrophosphate plus one mole of orthophosphate under all conditions when allowance is made for the concomitant hydrolysis of the pyrophosphate.

7. When the trimetaphosphate anion is hydrolyzed in strongly alkaline solution, it gives sodium tripolyphosphate.[66] The structure of the trimetaphosphate ring has been demonstrated by x-ray, and the first step in its hydrolytic degradation should be a straight three-membered chain as observed.

It should be noted that hydrolysis of long chain phosphates (a subject which will be discussed in Chapt. 12) in neutral solution leads to the formation of trimetaphosphate. This hydrolysis is very difficult to understand, in view of the long chain structure. Since there is considerable evidence to back up the idea that the molecule-ions of the phosphates in question really are long chains, we must conclude that straightforward, unsophisticated interpretations of hydrolysis data—and indeed chemical reactions in general—in terms of structure are very suspect. In truth, structural information obtained from reaction products appertains merely to the activated complex, which may only be present as an infinitesimal fraction of the reactants.

A report of "polymeric" sodium tripolyphosphate has appeared in the patent literature.[67] The polymeric nature of the sodium tripolyphosphate made by the described procedure was based on a misinterpretation of the kind of solubility data which are presented in Figure 10-20 and on cryoscopic measurements in sodium sulfate decahydrate. Repetition and a more careful analysis[68] of the cryoscopic work have shown that the falsely high values of the molecular weight described in the patent can be attrib-

[65] J. R. Van Wazer, E. J. Griffith, and J. F. McCullough, *J. Am. Chem. Soc.*, **77**, 387 (1955); J. P. Crowther and A. E. R. Westman, *Can. J. Chem.*, **32**, 42 (1954).

[66] E. Thilo and R. Rätz, *Z. anorg. Chem.*, **258**, 33 (1949).

[67] C. S. King, U. S. Pat. 2,419,148 (1947, assigned to Blockson Chemical Co.).

[68] F. E Hubbard, J. S. Metcalf, and W. R. Horlacher, unpublished data of the Monsanto Chemical Co

uted to the use of too large a sample of the $Na_5P_3O_{10}$, which has a low solubility in the $Na_2SO_4 \cdot 10\ H_2O$. (Sample weights of the order of 0.5 g. of $Na_5P_3O_{10} \cdot 6\ H_2O$ per 100 g. of $Na_2SO_4 \cdot 10\ H_2O$ and 1.0–1.5 g. of anhydrous $Na_5P_3O_{10}$ per 100 g. of $Na_2SO_4 \cdot 10\ H_2O$ give true values of the molecular weight, unaffected by poor dissolution of the tripolyphosphates.) When the solubility limit is not exceeded, all samples of $Na_5P_3O_{10}$ exhibit the expected molecular weight by this cryscopic method.

Preparation of Forms I and II and Mechanism of Dehydration of Precursors

Although methods of preparation[69] of pure $Na_5P_3O_{10}$-I and pure $Na_5P_3O_{10}$-II have often been simply described in the literature, it is a very difficult job to obtain a sample of either form which is not contaminated with at least several per cent of the other form plus varying amounts of tetrasodium pyrophosphate and crystalline sodium metaphosphates. Under some conditions, appreciable amounts of amorphous material are also present. In general, however, it can be said that it is much easier to make relatively pure Form II in the laboratory than to make relatively pure Form I.

As is the usual case with condensed phosphates, a large number of starting materials can be employed in preparing sodium tripolyphosphate. However, the starting material which has been used the most—both in the laboratory and in manufacturing procedures—has been the orthophosphate composition obtained by drying an orthophosphate solution containing approximately five moles of Na_2O to three moles of P_2O_5. The term "approximately" is used here because most manufacturers of sodium tripolyphosphate throughout the world employ a slight excess of Na_2O in their product to prevent the formation of turbidity due to small amounts of Maddrell's salts (Forms II and III of $NaPO_3$). In any event, at this composition, the solid orthophosphate precursor of sodium tripolyphosphate turns out to be an intimate mixture of the anhydrous double salt $Na_3H_3(PO_4)_2$, plus anhydrous Na_2HPO_4, and more or less of $Na_2HPO_4 \cdot 2\ H_2O$. The exact composition of $Na_5P_3O_{10}$ corresponds to an equimolar mixture of $Na_3H_3(PO_4)_2$ and Na_2HPO_4, regardless of the amount of hydration.

The following qualitative conclusions[70,71] have been reached on the

[69] For example, R. N. Bell, *Inorganic Syntheses*, ed. L. F. Audrieth, McGraw-Hill Book Co., New York, 1950, Vol. III, Chapt. V, pp. 101–03

[70] P. G. Arvan and J. R. Van Wazer, unpublished data of the Monsanto Chemical Co.

[71] J. W. Edwards and A. H. Herzog, *J. Am. Chem. Soc.*, **79**, 3647 (1957).

basis of a large number of calcination studies, carried out on the orthophosphate mixture described above, at various rates of heating to final temperatures in the range of 100–615°C.

1. Below 175°C., all of the P_2O_5 remains as orthophosphates. After heating for many days, x-ray examination of cooled samples shows only the double salt $Na_3H_3(PO_4)_2$ plus Na_2HPO_4, and sometimes some $Na_2HPO_4 \cdot 2\ H_2O$ (below 95°C.).

2. In samples which have been heated in the temperature range of 175–250°C. and then cooled, the Na_2HPO_4 and half of the $Na_3H_3(PO_4)_2$ is found as crystalline $Na_4P_2O_7$. This means that the disodium phosphate—whether or not it appears in the form of the double salt with the monosodium phosphate—goes to tetrasodium pyrophosphate. If the material is retained in this temperature range for a long period of time, the conversion to crystalline $Na_4P_2O_7$ is essentially complete. For rapid heating rates, such as are usually used in the preparation of sodium tripolyphosphate, only a small proportion of crystalline $Na_4P_2O_7$ is found to form while passing through this range of temperature. In this same temperature range of 175–250°C., the monosodium orthophosphate part of the $Na_3H_3(PO_4)_2$ double salt converts to $Na_2H_2P_2O_7$. Thus, for samples which are held for a long time in this temperature range, one obtains relatively good conversion to a mixture of two moles of crystalline $Na_4P_2O_7$ plus one mole of crystalline $Na_2H_2P_2O_7$. The $Na_4P_2O_7$, however, crystallizes at a considerably faster rate than does the $Na_2H_2P_2O_7$.

3. At a temperature around 200°C., anhydrous $Na_5P_3O_{10}$ starts to form at an appreciably fast rate, and at 300°C. the rate is sufficiently rapid under most experimental conditions so that there is practically complete conversion in several minutes' time. The lowest temperature at which the slow formation of crystalline $Na_5P_3O_{10}$ has been detected is 150°C. When the orthophosphate mixture is heated to a final temperature in the range of 350–400°C., most of it is converted to $Na_5P_3O_{10}$-II.

4. Under normal conditions in which the orthophosphate mixture is heated at a reasonable rate from room temperature to a final temperature in the range of 450–615°C. and then cooled, it is found that in the range of 450–500°C. there is a rather rapid transition of Form II of the $Na_5P_3O_{10}$ to Form I. This transformation is usually not complete, and it is commonly found that material heated to 500°C. or above still contains 5–30% of the $Na_5P_3O_{10}$ as Form II.

In Figures 10-17 and 10-18, data are presented from a comprehensive experiment in which the orthophosphate mixture, which, by the way, consists of 45.8 mole-% of $Na_3H_3(PO_4)_2$ and 54.2 mole-% of Na_2HPO_4,

was heated to 250°C.[71] The information concerning the composition during the course of the reaction was obtained on cooled samples by chromatographic analyses supplemented by quantitative x-ray studies. The chromatographic analysis divided the total P_2O_5 in each sample into that found as ortho-, pyro-, tripoly-, and higher polyphosphates, and as trimeta- and tetrametaphosphate rings, whereas the x-ray analysis showed

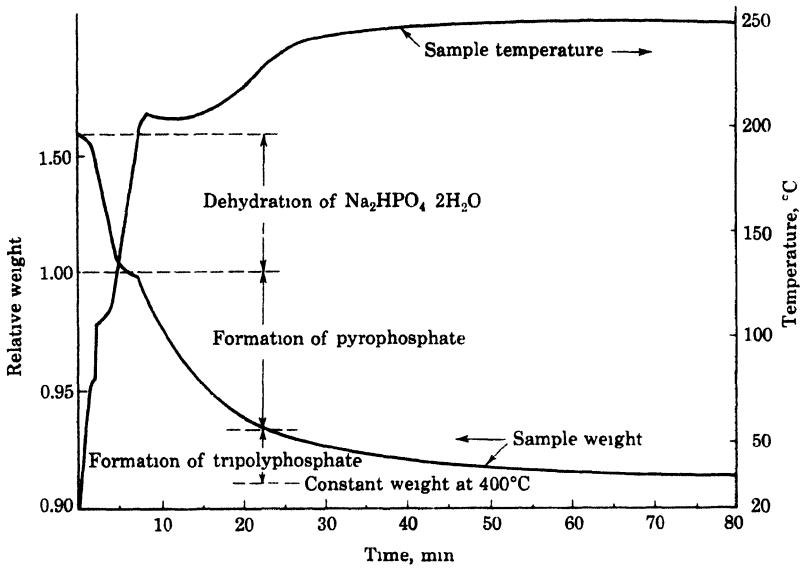


Fig. 10-17. Weight loss and temperature as a function of time for a sample of orthophosphate being converted to sodium tripolyphosphate. See Figure 10–18 for the accompanying analysis of the changing sample.

how much of these various constituents were present in crystalline form and exactly what crystalline form was there. Examination of Figure 10-18 shows that the crystalline orthophosphates, $Na_3H_3(PO_4)_2$ and the Na_2HPO_4, disappeared in such a manner that their proportions remained approximately constant. It should also be noticed that there was a considerable build-up of orthophosphate in the amorphous* material, with the concentration of amorphous orthophosphate reaching a maximum

* The amount of amorphous orthophosphate was measured with reasonable precision by subtracting the sum of crystalline orthophosphates determined by x-ray from the total amount of orthophosphates determined chromatographically. The same procedure was carried out for the pyro- and tripolyphosphates.

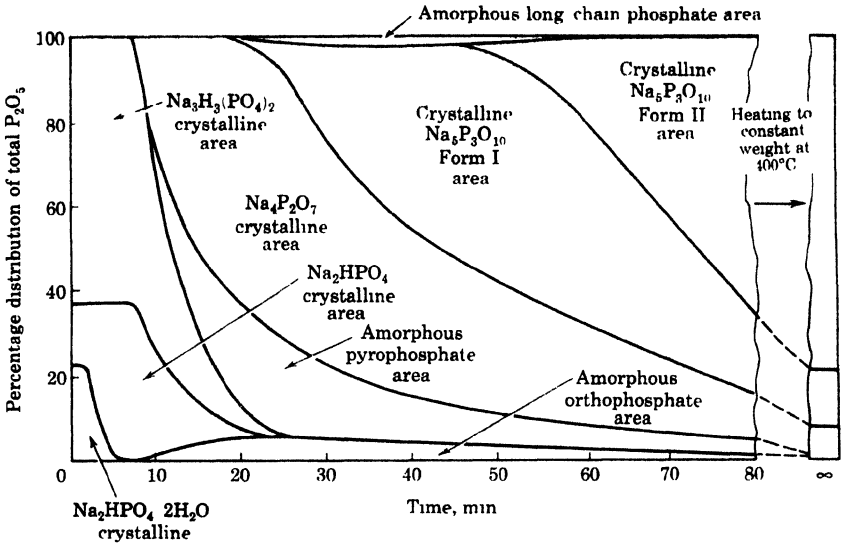


Fig. 10-18. Cumulative plot of the change of composition with time on converting an orthophosphate mixture to sodium tripolyphosphate. A coarsely granular starting material was used. The lines in this plot separate areas corresponding to the constituents noted.

of 9.3% of the total P_2O_5 at a temperature of about 229°C. The first step in the over-all process is the conversion of ortho- to pyrophosphate, which was found to reach a maximum amount of 80.3% of the total P_2O_5 when the temperature went to 229°C. As can be noted from Figure 10-19, the only pyrophosphate to crystallize was the tetrasodium salt, which means that the pyrophosphate in the amorphous phase was acidic, corresponding roughly to the composition $Na_2O \cdot H_2O \cdot P_2O_5$. The amount of tripolyphosphate in the amorphous form, on the other hand, was found to be undetectably small.

Another interesting anomaly appearing in Figure 10-18 is that the high-temperature form (Form I) of sodium tripolyphosphate became evident at the relatively low temperature of 235°C. and then was found to go through a maximum and disappear by conversion to Form II. This is an example of the Gay-Lussac Ostwald Step Rule (sometimes called the law of successive reactions) which says that an unstable form is usually produced before the stable form appears in the case of substances exhibiting several forms. The formation of $Na_5P_3O_{10}$-I at temperatures considerably below its equilibrium transition to Form II has been noted in a number of

studies carried out at Monsanto. It is found that the Form I build-up at low temperatures depends on particle size, with the rate of formation of Form I being greatest for coarse particles of the orthophosphate starting material. These results have led to the conclusion that the free energy of the activated complex for the formation of Form I (probably by the reaction of crystalline $Na_4P_2O_7$ with the amorphous, acidic mixture of pyro- and orthophosphates) is of the same order of magnitude or lower than the free energy of the activated complex for the formation of Form II. This means that the high-temperature, crystalline variety of sodium tripolyphosphate can appear in materials which have never been heated to the temperature above which this form is stable! Because of this and the essentially unidirectional transformation of Form II into Form I, it is extremely difficult to determine the equilibrium transition temperature between the two forms. However, studies in the presence of small amounts of water at high pressures carried out by Morey[18] show that the transition must lie between 409°C. and 415°C. This transition is unusual in that $Na_5P_3O_{10}$-I made by tempering $Na_5P_3O_{10}$-II above the transition temperature commonly will not reconvert to $Na_5P_3O_{10}$-II when tempered—even for a very long time—below the transition temperature.[4,10] However, if the $Na_5P_3O_{10}$-I is obtained from the glass, it can be tempered to Form II when held at temperatures below the transition point. This fact, coupled with the information that the Form I which appears during the low-temperature conversion of orthophosphates reconverts to Form II, surely indicates that the tempering of Form I into Form II is catalyzed by the presence of amorphous material. Presumably, the Form I → Form II conversion proceeds by dissolution into the amorphous phase.

Formation of crystalline $Na_2H_2P_2O_7$ in samples which were held at temperatures in the range of 175–250°C. (see item 2 in the listing of qualitative conclusions concerning dehydration of the orthophosphate composition corresponding to 5 Na_2O/3 P_2O_5) is simply crystallization from the acidic, amorphous material described in Figure 10-18. Two other crystalline materials which can appear at other temperatures and apparently form from the acidic amorphous phase are Maddrell's salt ($NaPO_3$-II and $NaPO_3$-III) and sodium trimetaphosphate ($NaPO_3$-I). The amount of Maddrell's salt can be maximized by carrying out slow conversions in the temperature range of 300–400°C.; and the sodium trimetaphosphate appears to form most rapidly in the temperature range of 400–500°C. It is believed that the rate of crystallization of Maddrell's salt is primarily limited by the formation and growth of its crystals, whereas, on the other hand, the sodium trimetaphosphate seems to form because of segregation of the re-

actants into small pockets isolated from each other by the crystals of sodium tripolyphosphate. It is interesting to note that $NaPO_3$-I″ can be detected when the orthophosphate starting mixture is rapidly dehydrated in a vacuum above 400°C.

Much of the above information has been reported in an important paper by McGilvery and Scott,[72] who emphasized the role of water during the formation of sodium tripolyphosphate by calcination procedures. These authors pointed up the fact, which has been known[19] for many years, *e.g.*, that water acts as a catalyst for the various transitions involved in the over-all process. When orthophosphates are used as starting materials, a considerable amount of water is released by their dehydration, and thus the reactions, such as those shown in Figures 10-17 and 10-18 are partially catalyzed However, when completely anhydrous starting materials are used, the rate of conversion in the absence of water is very many times less than in the presence of water. Also, controlling the amount of water vapor during conversion by varying the depth of the bed or adding steam has a pronounced effect on the various rates involved in the over-all process and, hence, can give appreciable differences in products carried through a given course of heating. It is interesting to note that nitrates also act as catalysts to effect the conversion of orthophosphates to sodium tripolyphosphate.[73]

In all but the most recent literature, there has been considerable emphasis on the crystallite size of the orthophosphate starting material, since the variability in the product prepared under ostensibly similar conditions implied poor mixing of the starting material. This emphasis on having very finely divided and well mixed starting materials has led to the rather awkward preparation of sodium tripolyphosphate through the tempering of a chilled melt[74]—a process that is still being employed commercially in Germany. Although it is not meant to imply that particle size is not an important factor, the fact that the original orthophosphates can be completely converted to an amorphous material plus crystalline $Na_4P_2O_7$ which further react to give the tripolyphosphate shows

[72] J. D. McGilvery and A. E. Scott, *Can. J. Chem.*, **32**, 1100 (1955), also see refs. 12, 24, 35, and 36, which deal with the mechanism of the dehydration of other orthophosphates to form polyphosphates. The paper by W. Herr and E. Meyer-Simon, *Z. Naturforsch.*, **6b**, 462 (1951), in which radioactive phosphorus is employed in studying the formation of $Na_5P_3O_{10}$ does not yield much useful information.

[73] Chem. Fab. Budenheim, Ger. Pat. Appl. C-2116 (1951), translated into English in Research Information Service Rept. 95917.

[74] F. Bornemann and H. Huber, U. S Pat. 2,174,614 (1939, assigned to Chem. Wks. Albert).

that formation of an extremely fine-grained, well-mixed starting material is not a necessary prerequisite to good conversion.[75]

In coarse admixtures of orthophosphates and particularly in starting mixtures of crystalline pyrophosphates or starting mixtures containing crystalline metaphosphates, the particle size does play an important role, with better conversion being obtained with finer particles. Similarly, if large crystals of $Na_2H_2P_2O_7$ are allowed to form along with the $Na_4P_2O_7$, further conversion is greatly inhibited Furthermore, converted products in which there is a large proportion of crystalline metaphosphates counterbalanced by two times the equivalent number of moles of tetrasodium pyrophosphate cannot be further converted (to any extent) to sodium tripolyphosphate by further simple heat treatment, even for a long time at high temperatures.

It is interesting to note that the tripolyphosphate ion has been enzymatically synthesized in aqueous solution [76] This was carried out by reacting the pyrophosphate ion with adenosine diphosphate in the presence of adenylate kinase (myokinase) from beef muscle. The equilibrium is in the direction of the tripolyphosphate ion.

Preparation of the Hexahydrate and Purified $Na_5P_3O_{10}\cdot 6\ H_2O$

The hexahydrate of sodium tripolyphosphate can be precipitated from a concentrated aqueous solution of either Forms I or II of the anhydrous salt by saturating with sodium chloride.[69] It is also obtained by precipitating with a water-soluble organic material, such as acetone or ethanol.

The purification of sodium tripolyphosphate in the form of its hexahydrate has been carefully studied by the use of radioactive tracers.[77] As previously stated, most commercial preparations of sodium tripolyphosphate contain several per cent of tetrasodium pyrophosphate and a small amount of soluble and insoluble metaphosphates; and, with difficulty, these can be removed by recrystallization As long as the weight ratio of $Na_5P_3O_{10}/Na_4P_2O_7$ exceeds 7/3—and is preferably greater than 4/1—and there are only a few per cent of ring metaphosphate, the following purification procedure gives a high-quality sodium tripolyphosphate.

After removal of any insoluble metaphosphate by filtration, ethanol is gradually added to an aqueous solution containing 12–15% of the impure tripolyphosphate until one volume of ethanol has been added to four volumes of the phosphate solution. After stirring for thirty minutes, the

[75] For example, C. S. King, U. S. Pat. 2,419,147 (assigned to Blockson Chemical Co.) has described "flash drying" as a way to get an intimate mixture of reactants.

[76] I. Lieberman, *J. Biol. Chem.*, **219**, 307 (1956).

[77] O. T. Quimby, *J. Phys. Chem.*, **56**, 603 (1954). Also see ref. 81.

hexahydrate crystals are filtered off, washed twice with a 1/1 mixture of ethanol and water and then redissolved in a minimum amount of water, and the process repeated. After four or five crystallizations, when commercial sodium tripolyphosphate is employed as the starting material, the $Na_5P_3O_{10}\cdot 6\ H_2O$ crystals are air dried at room temperature at a relative humidity in the range of 40–60%. This gives a yield of approximately 40–45% (based on the weight of commercial tripolyphosphate originally taken) of $Na_5P_3O_{10}\cdot 6\ H_2O$ containing as little as 0.5% of impurity. Most of this remaining impurity is tetrasodium pyrophosphate, which appears to be formed by slight decomposition of the $Na_5P_3O_{10}\cdot 6\ H_2O$ crystals during the drying process. As described in a following section, these crystals decompose when they are dehydrated.

Physical Properties of Sodium Tripolyphosphates

The acidity of $H_5P_3O_{10}$ prepared by passing a solution of sodium tripolyphosphate through a cation exchange column has been measured.[78] One hydrogen is essentially completely dissociated, and the dissociation constants at infinite dilution of the other four hydrogen ions are $K_2 = 10^{-1.1}$, $K_3 = 10^{-2.30}$, $K_4 = 10^{-6.26}$, and $K_5 = 10^{-8.90}$

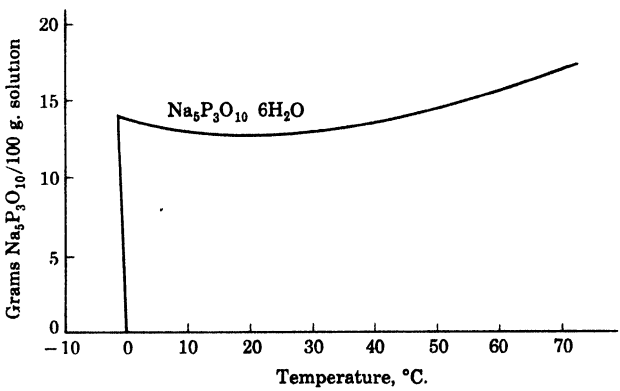


Fig. 10-19. Solubility of sodium tripolyphosphate as a function of temperature.

The solubility of sodium tripolyphosphate[77,79] in water as a function of temperature is shown in Figure 10-19. The eutectic temperature at which ice and $Na_5P_3O_{10}\cdot 6\ H_2O$ are in equilibrium with a saturated solution con-

[78] J. I. Watters, E. D. Loughran, and S. M. Lambert, *J. Am. Chem. Soc.*, **78**, 4855 (1956).

[79] J. R. Van Wazer, *Encyclopedia of Chemical Technology*, eds., R. C. Kirk and D. F. Othmer, Interscience Publishers, New York, 1953, p. 413.

taining 13.9% $Na_5P_3O_{10}$ is $-1.4°C$. It should be noted that, in the entire temperature range from 0 to 100°C., the saturating crystal phase is always the hexahydrate, and the anhydrous salt can, hence, not be crystallized from water, at least under atmospheric pressures.

As would be expected, because they are metastable forms when in contact with water at atmospheric pressure, the two anhydrous varieties of

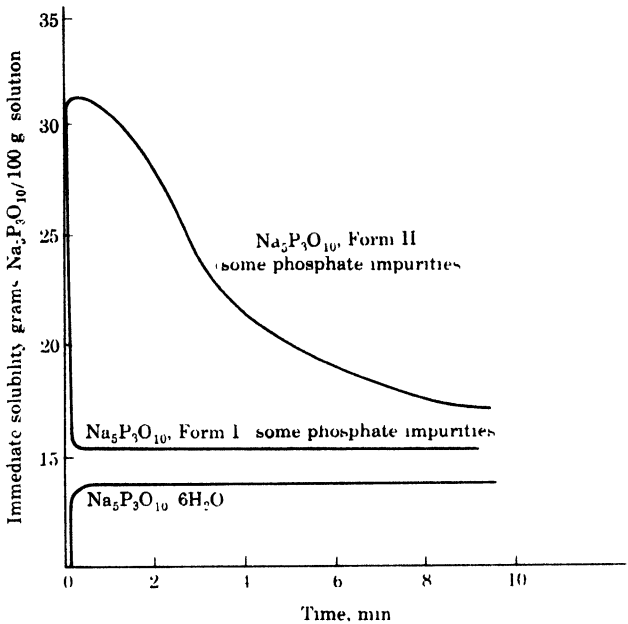


Fig. 10-20. Typical examples of the changing concentration of dissolved $Na_5P_3O_{10}$ in well-stirred slurries made up from 40 g. $Na_5P_3O_{10}$ and 60 g. H_2O. The shape of the curves depends on (1) stirring rate, (2) amount of added solid, (3) method of addition of the solid $Na_5P_3O_{10}$, and (4) its thermal history.

sodium tripolyphosphate are considerably more soluble than the hexahydrate. Although the equilibrium solubility of the two anhydrous forms has not been measured, a minimum value has been ascertained by slurrying these forms in water and measuring the change in concentration of dissolved $Na_5P_3O_{10}$ with time. A plot of two such experiments is given in Figure 10-20. As can be seen from these figures, the amount of dissolved $Na_5P_3O_{10}$ goes through a maximum and then decreases because of formation of the hexahydrate. The rate of nucleation of the hexahydrate seed crystals is

very much greater for slurries of Form I in water than for slurries of Form II of the anhydrous salt. Because of this, the curve shown in Figure 10-20 for Form I shows a rapid, nearly instantaneous drop in the concentration of dissolved solids The rate of hexahydrate nucleation is greatly affected by small amounts of substances other than anhydrous $Na_5P_3O_{10}$ -especially other phosphates which are normally found in reasonably pure anhydrous sodium tripolyphosphate. It is interesting to note that, even when solutions of the usual commercial sodium tripolyphosphate are seeded with hexahydrate crystals, the amount of dissolved phosphate remains high and does not decrease to the equilibrium solubility of $Na_5P_3O_{10} \cdot 6\ H_2O$, even after many hours. The purer the sodium tripolyphosphate, the more rapidly the concentration of dissolved phosphate decreases and the more closely the long-time solubility approaches the true solubility of the hexahydrate.

When the two anhydrous forms of sodium tripolyphosphate are dissolved in water, considerable heat is given off, whereas dissolution of the hexahydrate causes some cooling. The integral heat of solution[80] for solutions containing several per cent of $Na_5P_3O_{10}$ is -16.1 kcal./mole for Form I, -14.0 kcal./mole for Form II, and $+2.6$ kcal./mole for the hexahydrate This means that a mixture of about 85 mole % of the hexahydrate and about 15 mole % of the anhydrous $Na_5P_3O_{10}$ will dissolve without causing heating or cooling of the solution. This corresponds approximately to the hypothetical composition: $Na_5P_3O_{10} \cdot 5\ H_2O$.

As described below, under the section entitled Degradation of Sodium Tripolyphosphate, the hexahydrate cannot be dehydrated without some degradation at temperatures below 100–110°C. This means that the partial pressure of water over the hydrate usually does not correspond to an equilibrium pressure due to the reaction: $Na_5P_3O_{10} \cdot 6\ H_2O(s) \rightleftharpoons Na_5P_3O_{10}(s) + 6\ H_2O(g)$. Careful measurements of the partial pressure of water over $Na_5P_3O_{10} \cdot 6\ H_2O$ under conditions where hydrolysis is minimized show that the equilibrium pressure is low, ranging[81] from about 0.07 mm. of Hg at 25°C. to 0.8 mm. at 50°C.

The Form I variety of sodium tripolyphosphate is known as the "lumping variety," since under normal conditions, when added to poorly agitated water, it lumps or cements together.[82] The lumping of Form I causes

[80] J. D. McGilvery, *A.S.T.M. Bull.*, **191** (July issue), 22 (1953).

[81] C. Y. Shen, J. S. Metcalf, and E. V. O'Grady, *Ind. Eng. Chem.* (submitted for publication); B. C. Hafford, *Ind. Eng. Chem.*, **46**, 1938 (1954) gives much higher values not representing equilibrium.

[82] B. Raistrick, *Sci. J. Roy. Coll Sci*, **19**, 9 (1949); V. Mills, U. S. Pat. 2,712,529 (1950, assigned to Procter and Gamble)

pronounced effects in the crutching and handling of detergent slurries; therefore, considerable effort has been devoted to the problem of readily determining the ratio of Form I to Form II in the anhydrous material, and this ratio is carefully controlled in making the sodium tripolyphosphate utilized in the manufacture of spray-dried detergent formulations. On the other hand, Form II of sodium tripolyphosphate can be added to unagitated water without undue caking or lumping. The cause of this lumping of Form I is its extremely high solubility, which is due to the fact that Form I is more metastable than Form II in contact with water. The formation of hexahydrate crystals from the highly supersaturated solution results in a matting together of the entire mass by a mesh of $Na_5P_3O_{10} \cdot 6\ H_2O$ crystals.

Degradation of Sodium Tripolyphosphate

As has previously been discussed in Chapter 8, the hydrolytic degradation of the condensed phosphates in aqueous solution is extremely slow near neutral pH at room temperature. Thus, for sodium tripolyphosphate at 25°C. and pH 7, the half-life of the dissolved $Na_5P_3O_{10}$ is greater than a year. A nomograph[83] giving the half-life of the tripolyphosphate ion in solution as a function of temperature and pH is shown in Figure 10-21. This figure refers to tetramethylammonium tripolyphosphate dissolved in a solution containing tetramethylammonium bromide The data are given for the tetramethylammonium salt in the presence of swamping electrolyte because this is a good comparison standard for which rather complete data are available. It should be remembered that sodium ion exhibits an accelerating effect on the rate—due to the fact that it is somewhat complexed by the tripolyphosphate anion—and that the presence of other cations which form stronger complexes has an even greater effect on the rate than does sodium. For all practical purposes, however, the effect of changing cations and generally of varying the ionic atmosphere is small—causing a change of no more than several fold in the half-life. For comparison, it should be noted that the variation in half-life from boiling temperatures at low pH to freezing temperatures at high pH covers a 10-million-fold range!

In spite of the fact that the rate of hydrolysis in aqueous solution is slow under alkaline conditions, it is often found in practice that concentrated slurries of pentasodium tripolyphosphate undergo extremely fast degradation. Thus, for example, in heavy-duty detergent compositions which

[83] E. J. Griffith, from data by J. R. Van Wazer, E. J. Griffith, and J. F. McCullough, *J. Am. Chem. Soc.*, **77**, 287 (1955).

have been spray-dried under properly controlled conditions, 50–75% of the sodium tripolyphosphate originally added to the mix can be converted to pyro- and orthophosphates, even though the half-life of the tripolyphosphate ion in solution in the crutcher and accessory equipment is approxi-

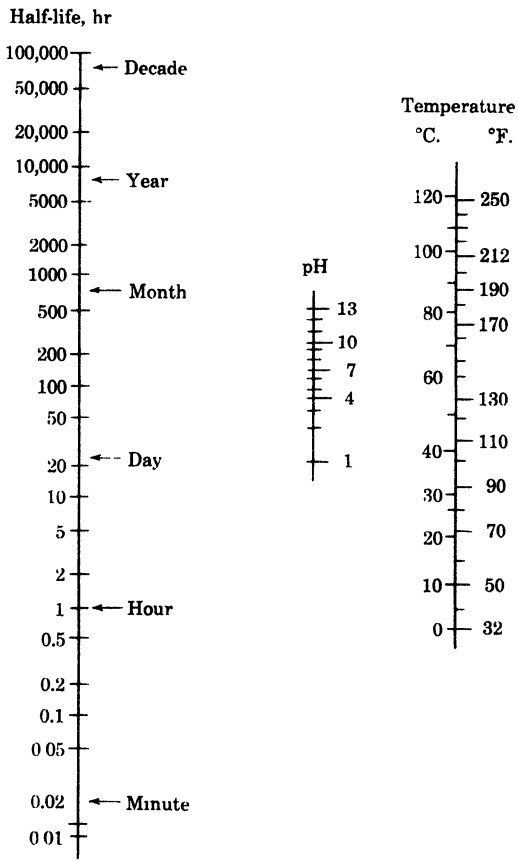


Fig. 10-21. Half-life of the tripolyphosphate ion as a function of pH and temperature. (Data refer to tetramethylammonium tripolyphosphate dissolved in 0.65 *N* tetramethylammonium bromide.)

mately 30 hr. and in the spray-drying tower (where it remains for about a second) is about 5 hr. Furthermore, the degradation product usually shows up as nearly all pyrophosphate, rather than the equimolar mixture of pyro- and orthophosphates which is obtained from hydrolysis in alkaline

solution. This means that the observed degradation is nearly wholly attributed to the dehydration of the hexahydrate crystals described below.

When $Na_5P_3O_{10} \cdot 6\,H_2O$ is dehydrated at temperatures below about 135°C., it is always found to undergo some degradation. At temperatures below about 100–110°C., the formation of anhydrous $Na_5P_3O_{10}$ has never been detected in a dehydrated sample Although the literature[84,85] on the subject of this dehydration is far from consistent in its interpretation, the experimental data present a rather straightforward picture which has been greatly clarified by the recent interpretation of Quimby.[77] It is found that, at temperatures below about 110°C., the decomposition product consists of crystalline $Na_4P_2O_7$ plus an amorphous mixture of acidic sodium ortho- and pyrophosphates Often, there is more than a 1:1 mole ratio of pyro- to orthophosphates, depending on the exact conditions of the dehydration. This is apparently due to a reorganization process involving the molecule-ions in the amorphous phase. A number of equations have been written to describe the degradation, but because of the presence of the amorphous phase and the probability of reorganization within it, such classical equations do not seem to be very meaningful.[81]

At temperatures above 120°C slow recondensation of the crystalline $Na_4P_2O_7$ with the amorphous ortho-pyro mixture takes place; and, as noted in the previous section dealing with the mechanism of dehydration of orthophosphates to form sodium tripolyphosphate, this recombination does not occur at a reasonably fast rate until the temperature is greater than 200°C. Direct dehydration of the hexahydrate to anhydrous $Na_5P_3O_{10}$-II appears to take place at temperatures in the range of 135–230°C. when the water is quickly flashed out of the hydrate However, there is also some concomitant degradation which has made it impossible to measure a transition pressure of H_2O at these temperatures.

Analysis of Sodium Tripolyphosphate

Because of its great commercial importance, considerable work has been devoted in the last few years to analytical methods specifically directed to the assay of commercial sodium tripolyphosphate. Quantitative x-ray techniques[82,86] have been developed for mixtures of Forms I and II with the hexahydrate and tetrasodium pyrophosphate plus sodium trimeta-

[84] E. Thilo and H. Seeman, *Z. anorg. u. allgem Chem.*, **267**, 65 (1951); E. Thilo, *Sitzber. deut. Akad. Wiss. Berlin, Kl. Math. u. allgem. Naturw.*, **1**, 1 (1952); O. T Quimby, *Chem. Revs.*, **40**, 141 (1947); also see refs. 70 and 74

[85] P. Bonneman-Bémia, *Ann. chim.*, **16**, 395 (1941).

[86] A. J. Mabis and O T. Quimby, *Anal. Chem.*, **25**, 1814 (1953).

phosphate and Maddrell's salt. In the most recent publication on this subject,[86] added magnesium oxide was used as an internal standard in the determination of mixtures of $Na_5P_3O_{10}$-I, $Na_5P_3O_{10}$-II, $Na_5P_3O_{10}\cdot 6\,H_2O$, and $Na_4P_2O_7$. These four compounds exhibit strong diffraction peaks for which there is little or no interference at values of 2θ equal to 29.1° (also 21.85°), 24.85°, 14.0°, and 26.45°C., respectively. Comparison of the intensities of these lines with calibration charts gives a quantitative measure of the amount of the respective constituent present Although the average deviation from the mean in replicate determinations is only several per cent, possible crystallite alignment is an indeterminate source of error present in all x-ray analyses This technique, with and without the magnesium oxide standard (ref. line: $2\theta = 43.0°$), has been extended to a number of other alkali metal phosphates,[87] and mixtures of all of the common crystalline phosphates can be quantitatively analyzed by x-ray diffraction. Generally, the x-ray technique will not pick-up constituents present to less than 1–4% of the total.

Another technique for the differential analysis of the condensed phosphates which is quite similar to x-ray diffraction is infrared analysis.[88] In this procedure the dry phosphate is mixed with potassium bromide and pressed into disks, the infrared absorption spectra of which are measured By comparing the intensities of certain absorption peaks, quantitative analyses of mixtures of Forms I and II of sodium tripolyphosphate, sodium pyrophosphate, and sodium trimetaphosphate are claimed to be carried out to a precision of ±0.5%, within the concentration range found in commercial sodium tripolyphosphate.

Because of the difficulty in running an x-ray or infrared machine for routine determination of the ratio of Form I to Form II in sodium tripolyphosphate, a thermal test has been developed at Procter and Gamble for this analysis. This procedure,[80,89] called the Temperature Rise Test, is based on the fact that in a glycerin-water mixture, the $Na_5P_3O_{10}$-I hydrates much more rapidly than does $Na_5P_3O_{10}$-II. When the test is carried out according to instructions,[89] the percentage of Form I is given by the following equation:

$$\text{Per cent } Na_5P_3O_{10}\text{-I} = 4\,[(\text{temp. rise in °C.}) - 6] \qquad (10\text{-}18)$$

The compounds usually found in commercial sodium tripolyphosphate in

[87] J. W. Edwards, unpublished information of the Monsanto Chemical Co.

[88] D. E. C. Corbridge and E. J. Lowe, *Anal. Chem.*, **27**, 1383 (1955).

[89] E. Karl-Kroupa, J. R. Van Wazer, and C. H. Russell, *Scott's Standard Methods of Chemical Analysis*, ed. N. H. Furman, 6th ed , D. Van Nostrand Co., New York (to be published).

addition to anhydrous $Na_5P_3O_{10}$ do not affect the Temperature Rise Test when present in their usual amounts. In particular, tetrasodium pyrophosphate has no effect when present to less than 50% of the sample.

A number of chemical assay procedures have been developed for commercial sodium tripolyphosphate.[90-93] Of these, the chromatographic technique[91] probably gives the greatest absolute accuracy, although the procedure[92] based on precipitation with tris(ethylenediamine)cobalt(III) ion gives a high degree of precision and probably sufficient accuracy for commercial samples. Other interesting analytical techniques[93] which have been applied to sodium tripolyphosphate are radioactive isotope dilution and anion-exchange chromatography.

Other Sodium Tripolyphosphates

Thus far, only one sodium acid tripolyphosphate, $Na_4HP_3O_{10} \cdot 1.5\ H_2O$, has been made in crystalline form.[94] This salt was precipitated with alcohol from a solution of $Na_5P_3O_{10}$ in acetic acid. The salt $Na_3H_2P_3O_{10}$, which has been reported in the literature, has never been crystallized and represents a classical description of some of the amorphous material found when orthophosphates are being converted to polyphosphates.

By removing various amounts of the sodium with a cation exchange resin and treating the resulting acid solution with ammonia, two sodium ammonium tripolyphosphates have been prepared.[95,96] One of these salts, $Na(NH_4)_4P_3O_{10}$, has been obtained as a dihydrate by precipitating with alcohol at about 4°C. and as a tetrahydrate by crystallizing from a small amount of hot water. The other salt of the formula $Na_3(NH_4)_2P_3O_{10} \cdot x\ H_2O$ can be made by slow crystallization of the oily, amorphous material precipitated by alcohol from a solution having the proper ratio of sodium to ammonium ions.

[90] W. R. Cale, *Can. Chem. Process Inds.*, **32**, 741 (1948); B. Raistrick, F. J. Harris, and E. J. Lowe, *Analyst*, **76**, 230 (1951); R. N. Bell, A. R. Wreath, and W. T. Curless, *Anal. Chem.*, **24**, 1997 (1952); W. Dewald and H. Schmidt, *Z. anal. Chem.*, **137**, 178 (1952); W. Dewald, H. Schmidt, and K. H. Neeb, *ibid.*, **138**, 91 (1953); W. Dewald, *Fette u. Seifen*, **56**, 105 (1954); L. E. Netherton, A. R. Wreath, and B. N. Bernhart, *Anal. Chem.*, **27**, 861 (1955).

[91] E. F. Karl-Kroupa, *Anal. Chem*, **28**, 1091 (1956).

[92] H. W. McCune and G. J. Arquette, *Anal. Chem.*, **27**, 401 (1955); H. J. Weiser, *ibid.*, **28**, 477 (1956).

[93] J. A. Grande and J. Beukenkamp, *Anal. Chem*, **28**, 1497 (1956); H. J. Weiser, *J. Am. Oil Chem. Soc.*, **84**, 124 (1957); W. G. Spangler, D. E. Howes, Jr., and J. A. Kish, *ASTM Bull.*, Feb. 1958, p. 61; O. T. Quimby, A. J. Mabis, and H. W. Lampe, *Anal Chem.*, **26**, 661 (1954).

[94] H. Huber, *Z. anorg. u. allgem. Chem.*, **230**, 123 (1936).

[95] R. Klement, *Z. anorg. Chem.*, **260**, 18 (1949).

[96] E. Thilo and R. Rätz, *Z. anorg. Chem.*, **258**, 33 (1949).

In addition to the sodium tripolyphosphates listed above, there are a number of double salts of sodium with multiply charged metal ions, which are obtained by adding a soluble salt of the metal to a solution of $Na_5P_3O_{10}$ in order to form a precipitate. These salts are reviewed in Table 10–4.

Potassium Tripolyphosphate

The preparation of $K_5P_3O_{10}$ is carried out very similarly to the preparation of $Na_5P_3O_{10}$. As is generally the case with phosphates, the potassium salt is more soluble and more hygroscopic than the sodium salt. The solubility[97] of $K_5P_3O_{10}$ in water is not known definitely, but it is very great, being at least 180 g./100 g. H_2O at 25°C. The solubility is difficult to determine because (1) the salt peptizes itself upon dissolution, thus forming a cloudy suspension, and (2) upon dehydration of a solution, a gummy, uncrystallized mass is obtained. Such a glue-like mass does not crystallize after standing for many days The integral heat of solution is 12 kcal./mole in 100 moles of water.

Potassium tripolyphosphate is insoluble in organic solvents, with less than 0.5 g. being dissolved by 100 g. of anhydrous ethanol. The solubility[44] in ethanol-water mixtures is shown in Figure 10–16. When ethanol or other water-soluble organic substances are used to precipitate $K_5P_3O_{10}$ from aqueous solution, an oil rather than a crystalline precipitate is formed. Upon prolonged exposure to atmospheric moisture, $K_5P_3O_{10}$ picks up enough water to form a plastic mass which then further liquefies in extremely humid environs.

A potassium acid tripolyphosphate, $K_3H_2P_3O_{10} \cdot 1\text{–}2\ H_2O$ has been mentioned in the literature.[99] This substance crystallized after being precipitated as an oil from a solution of $K_5P_3O_{10}$ in acetic acid.

Tripolyphosphates Made by Precipitation from Solution

As is the general case with chain phosphates, heavy metal and multiply charged cations give precipitates with soluble tripolyphosphates. Often these precipitates include the cation of the soluble salt, so that, if the precipitation is made from a solution of sodium tripolyphosphate, the precipitate will contain some sodium ion. A considerable amount of qualitative information concerning such precipitates can be found in the early litera-

[97] F. E. Hubbard, technical information of the Monsanto Chemical Co.

[98] P. Bonneman, *Compt. rend.*, **209**, 214 (1939).

[99] W. Dewald, *Angew. Chem.*, **67**, 654 (1955).

ture.[1,60] In papers such as the original article on polyphosphates by Fleitmann and Henneberg,[1] a number of "double salts" exhibiting the tripolyphosphate composition are described. Unfortunately, the investigators of that time often did not clearly distinguish between crystalline and amorphous precipitates and used doubtful preparations of sodium tripolyphosphate. Therefore, it is hard to tell whether the "double salts" are merely complicated mixtures having no definite composition.

A listing of crystalline tripolyphosphates formed by precipitation from aqueous solution (in most cases an aqueous solution of pentasodium tripolyphosphate) is given in Table 10-4. In this table the publications on this subject before 1895 have been ignored, and only those tripolyphos-

TABLE 10-4
Crystalline Tripolyphosphates Formed by Precipitation[a] from Aqueous Solution

Salt	Remarks	Reference
$Na_6P_3O_{10}\cdot H_2O\cdot H_2O_2$	Sol. salt made by slow evapn. Cannot be pptd. by alcohol	85
$Na_3(NH_4)_2P_3O_{10}\cdot aq.$		
$Na(NH_4)_4P_3O_{10}\cdot 2\ H_2O$	Sol. salts made by evapn.	95,96
$Na(NH_4)_4P_3O_{10}\cdot 4\ H_2O$		
$Na_3MgP_3O_{10}\cdot 13\ H_2O$	Small colorless cryst.	60b,85
$NaCa_2P_3O_{10}\cdot 4\ H_2O$	Fine crysts. from very dilute solns. Crvst. to x-ray	98,85
$NaSr_2P_3O_{10}\ 7\ H_2O$	Well-formed crvst. Crvst. to x-ray	85
$Na_3CuP_3O_{10}\cdot 12\ H_2O$	Bluish cryst.	60b,85
$Cu_5(P_3O_{10})_2\cdot 13\ H_2O$	Unstable crvst., amorphous ppt. often formed	60b,85
$Na_3ZnP_3O_{10}\ 11\ 5\ H_2O$	Colorless transparent crvst. often formed in tufts	98,85
$NaZn_2P_3O_{10}\ 9\ 5\ H_2O$	Colorless prismatic needles. Probably triclinic. Loses H_2O at 80°C in few hr.	60,2,85
$Na_3CdP_3O_{10}\cdot 12\ H_2O$	Well-formed white needles	60a,64,85
$NaCd_2P_3O_{10}\cdot 7\ H_2O$	Poorly crystallized powder showing cryst. structure by x-ray	98,85
$Na_6Pb(P_3O_{10})_2\cdot 14\ H_2O$	White cryst. showing good structure by x-ray	85
$Na_2CrP_3O_{10}\cdot 6\ H_2O$	Small dk. green crvst.	60a,64,85
$Na_3MnP_3O_{10}\cdot 12\ H_2O$	Small reg. prisms	60,98,85
$Na_3CoP_3O_{10}\cdot 12\ H_2O$	Regular prisms, rose-red	60,85
$K_3CoP_3O_{10}\cdot aq.$	Small cryst. from adding a Co salt to $K_5P_3O_{10}$	85
$Na_3NiP_3O_{10}\cdot 12\ H_2O$	Regular prisms, green	60,85,96
$NaNi_2P_3O_{10}\cdot aq.$		96

[a] All salts insoluble in water unless otherwise noted.

phates which the literature declares to be truly crystalline are included. In addition to these crystalline compounds, it is interesting to review some known amorphous compositions which can be readily prepared and have also been described in the literature. One of the best known of these amorphous compositions is formed when salts of the alkaline earth metals are added to solutions of sodium tripolyphosphate. This amorphous precipitate has the general formula $Ae_5(P_3O_{10})_2$, where Ae stands for Be, Ca, Ba, or Sr. Bonneman-Bémia[85] has shown that these precipitates are noncrystalline to x-ray. Another related precipitate is $NaBeP_3O_{10} \cdot 5\,H_2O$, which this same author has also shown to be amorphous to x-rays. A number of lead salts have been described in addition to the crystalline one given in Table 10–4, but they have either been amorphous or could not be prepared by investigators other than the persons who originally described them. The case of iron is an interesting one in that, when ferric sulfate is added to a solution of sodium tripolyphosphate, the only crystalline phosphate obtained is ferric pyrophosphate! Presumably there is formation of a considerable amount of hydrated ferric oxide which is known to catalyze strongly the degradation of the condensed phosphates. A salt $Na_3Fe''P_3O_{10} \cdot 11.5H_2O$ has been investigated by several authors, but this material appears to be amorphous and may have a variable composition. Also, two salts of manganese, $NaMn_2P_3O_{10} \cdot xH_2O$ and $Mn_5(P_3O_{10})_2$, have been described, but the existence of the first and the crystallinity of the second are questionable.

Other Tripolyphosphate Compositions

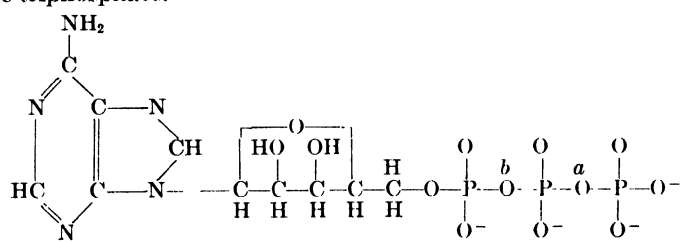
A large number of preparations of the general formula $5\,M_2O \cdot 3\,P_2O_5$ have been made by mixing metal oxides and metal salts having volatilizable anions with phosphoric acid and then heating. Some of these materials are amorphous and others exhibit x-ray powder patterns of crystals. However, in most cases, it is not known whether the crystalline materials are mixtures or single compounds, and therefore no further discussion of such preparations will be given here. It is common practice to call such preparations tripolyphosphates when, indeed, they should be dubbed salts of the tripolyphosphate composition.

Organic Tripolyphosphates

The only reliable procedure for making normal esters of tripolyphosphoric acid which has been employed to date is the reaction of silver tripolyphosphate with alkyl halides. By use of this technique, pentaethyl

tripolyphosphate has been prepared.[100] The P—O—P bonds in this ester—as in tetraethyl pyrophosphate—are relatively reactive and undergo quite rapid scission through (1) hydrolysis, (2) ammonolysis, and (3) reaction with organic bases and their salts (*e.g.*, aniline and guanidine carbonate). Presumably, this is again attributable to the three covalent bonds from each PO_4 group causing the PO_4 group to act as a branching point (Antibranching Rule).

The tripolyphosphates of major biological interest are adenosine triphosphate and the related 5′-ribonucleotides. The adenosine compound has been synthesized[101] in the same manner as adenosine pyrophosphate shown in equations 10-7 and 10-8. Since the organic radical is attached to a terminal PO_4 group, there is no enhancement of the reactivity of the P—O—P linkages. In fact, the usual point of scission in biological processes is *a* in 10–19, rather than point *b* which lies closest to the organic part of the molecule-ion. The adenosine triphosphate is shown below. Other well-known biological derivatives of the tripolyphosphate moiety are inosine triphosphate, cytidine triphosphate, uridine triphosphate, and guanosine triphosphate.



(10-19)

The complexing ability of adenosine mono-, di-, tri-, and tetraphosphates has been studied for the alkali metal and alkaline earth metal ions.[102] As expected, the longer the polyphosphate chain, the better the complexing as measured by pH titration. Also the alkaline earth metal ions were much more strongly complexed than the alkali metal ions.

TETRAPOLYPHOSPHATES

As shown in Figure 10-7, there is a crystalline tetrapolyphosphate in the PbO–P_2O_5 system. In addition, there is also a crystalline tetrapoly-

[100] A. Hood and W. Lange, *J. Am. Chem. Soc.*, **72**, 4956 (1950); R. Rätz and E. Thilo, *Z. anorg. u. allgem. Chem.*, **272**, 333 (1953).

[101] J. Baddiley, A. M. Michelson, and A. R. Todd, *Nature*, **161**, 761 (1948); also see ref. 53 and H. G. Khorana, *J. Am. Chem. Soc.*, **76**, 3517 (1954).

[102] R. M. Smith and R. A. Alberty, *J. Am. Chem. Soc.*, **78**, 2376 (1956); *J. Phys Chem.*, **60**, 180 (1956).

phosphate in the BaO–P_2O_5 system.[7] Although the phase diagram for this latter system has not yet been worked out, a polyphosphate having a unique x-ray pattern was definitely detected. Isolation of this polyphosphate and conversion to the sodium salt showed that it was a tetrapolyphosphate, because it exhibited only the spot for the tetrapolyphosphate ion in paper chromatography.

Proof that these two salts are truly linear tetrapolyphosphates is very much the same as the proof of structure of the tripolyphosphate anion presented earlier in this section. Of the seven proofs given for the tripolyphosphate anion, numbers 1, 2, 4, and a sophisticated variant of 5 apply to the lead tetrapolyphosphate and the sodium salt derived from it.

The crystalline barium and lead tetrapolyphosphates described above can be converted to soluble forms by the use of cation exchange resins or by metathesis with an alkali metal salt, the anion of which forms very insoluble precipitates with the cation of the tetraphosphate. Thus sodium tetrapolyphosphate, $Na_6P_4O_{13}$, is slowly produced in solution by reacting the barium salt with the sodium form of an ion exchange resin or by precipitating lead carbonate through addition of sodium carbonate to a slurry of the lead salt. In fact, this has been a main step in proving the structures of the lead and barium salts. The alkaline hydrolysis of sodium tetrametaphosphate has also been used to prepare sodium tetrapolyphosphate. This reaction has been studied by several authors,[103] who have been able to get reasonably good yields of $Na_6P_4O_{13}$ in solution.

Numerous attempts to prepare crystalline sodium tetrapolyphosphates have ended in failure, since the usual precipitation procedures have given an oil which would not crystallize.[104] The first soluble tetrapolyphosphates to be crystallized[77] from solution were salts of organic bases—tetraacridinium tetrapolyphosphate and hexaguanidinium tetrapolyphosphate. In addition, ammonium tetrapolyphosphate has also been crystallized.[104] The tetraacridinium and ammonium salts undergo decomposition during storage, but the hexaguanidinium tetrapolyphosphate appears to be more stable. All of these salts are very soluble in water, with the solubility probably being over 50% by weight in each case.

The nuclear magnetic resonance spectrum of the tetrapolyphosphate anion in a solution of crystalline ammonium tetrapolyphosphate is shown

[103] E. Thilo and R. Ratz, *Z. anorg. Chem.*, **260**, 255 (1949); A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951); A. E. R. Westman, A. E. Scott, and J. T. Pedley, *Chemistry in Can.*, **4**, 35 (1952); also see ref. 70.

[104] A single preparation of sodium tetrapolyphosphate in crystalline form has been described by A. E. R. Westman *et al.* (see Anon., *Can. Chem. Processing*, **June 2 issue**, 74 (1955)), but these investigators have not been able to repeat the preparation.

in Figure 10-16. This spectrum offers a good proof of the linear structure of the $P_4O_{13}^{6-}$ anion, since there are only ends and middles in the structure, with equal amounts of each (the isotetropoly would have three ends to one branch PO_4 group). In addition, the splitting of both the end and middle peaks into doublets substantiates the structure (see last paper listed in ref. 22).

Adenosine tetraphosphate has been isolated from muscle,[105] where it is found with the other adenosine phosphates. It is interesting to note that adenosine tetraphosphate does not act as a phosphate donor in some of the well-known reactions of adenosine triphosphate—reactions such as the formation of glucose-6-phosphate with hexokinase (see p. 595), or phosphate transfer to adenosine-5-phosphate in the presence of adenylate kinase.

INDIVIDUAL POLYPHOSPHATES LARGER THAN THE TETRA

The crystalline calcium phosphate called trömelite has recently been shown to be a pentapolyphosphate.[16a] This structure proof is based on paper chromatography of an ethylenediaminetetraacetate solution of the trömelite. The fact that trömelite represents a considerable region of crystalline solid solution in Figure 10-7 is no reason for doubting the pentapolyphosphate formulation since other calcium phosphates (*e.g.*, $Ca_2P_2O_7$) also give crystalline solid solutions.

Ion exchange and paper chromatography offer the only two reliable procedures for identifying individual species of short chain polyphosphates. So far, the ion exchange technique has not been developed to the point where its potentialities have been utilized for this purpose. However, studies with paper chromatography have demonstrated that this method is very suitable for chain phosphates smaller than the dodecapolyphosphate. In Figure 10-22, R_f values[6,91,106] are plotted as a function of chain length for the chromatographic solvents on which such data are available.

The presence of the various moderately sized chain polyphosphates can be ascertained by paper chromatography, and quantitative analysis for the amount of the various constituents present can also be carried out by this procedure. Thus, in determining the purity of an exploratory sample of a previously uncrystallized pyrophosphate and investigating various ways of purification, this technique is invaluable. After the sample has been obtained in pure form, additional structure proofs can be obtained by using

[105] I. Lieberman, *J. Am. Chem. Soc.*, **77**, 3373 (1955); D. H. Marrian, *Biochim. et Biophys. Acta*, **12**, 492 (1953); *ibid.*, **13**, 278 (1954).

[106] H. Grunze and E. Thilo, *Sitzber. deut. Akad. Wiss. Berlin, Kl. Math. u. allgem Naturw.*, **5**, 1 (1953), A. E. R. Westman, private communication.

(1) pH titration for end groups, (2) nuclear magnetic resonance determination of end group/middle group ratio, and (3) cryoscopy in sodium sulfate.

There are several ways in which, sometime in the future, individual polyphosphate species higher than the pentapolyphosphate might be obtained in more than trace amounts as pure substances. Firstly, it is quite possible that rings larger than the tetrametaphosphate might be isolated in con-

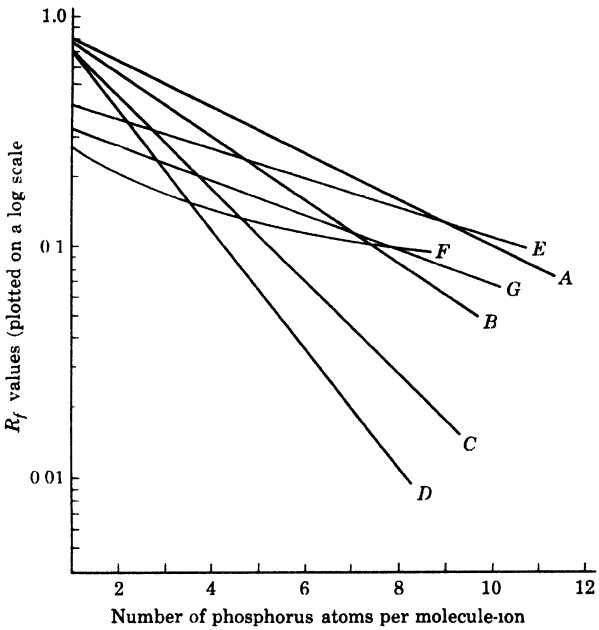


Fig. 10-22. R_f values for chain phosphates in different solvents. See Table 10-5 for the experimental conditions leading to these curves. R_f is the ratio of the distance traveled by the spot to the distance traveled by the solvent front in the chromatogram

centrated form. In this case, hydrolytic scission could give solutions from which crystalline precipitates might be formed. Secondly, there is also the possibility that, when the phase diagrams of various metal oxides with P_2O_5 have been more fully investigated, a hexapolyphosphate or even higher polyphosphate will be found. There seems to be no way to predict whether or not such a finding will be made, since the occurrence of a given crystalline substance is highly dependent upon the lattice energies involved, and since there is apparently no reason why a particular metal

TABLE 10-5
Chromatographic Data Corresponding to the R_f Values of Figure 10-22

Curve in Fig. 10-22	Chromatographic solvent	Filter paper
A	70 ml. isopropyl alcohol 20 ml. trichloroacetic acid (25 wt. %) 10 ml. water 0.3 ml. conc. ammonia	Schleicher and Schull 589 (green), batch 46
B	As above, but using 20% trichloroacetic acid	Schleicher and Schull 2040 (washed with dilute HCl and then with distilled H_2O)
C	75 ml. isopropyl alcohol 25 ml. water 5 g. trichloroacetic acid 0.3 ml. ammonia (20 wt. %)	As preceding
D	As above	Schleicher and Schull 589 (orange ribbon)
E	30 ml. isobutyl alcohol 30 ml. absolute ethyl alcohol 39 ml. water 1 ml. ammonia (25%)	Schleicher and Schull 2040 (washed with dilute HCl and then with distilled H_2O)
F	40 ml. isopropyl alcohol 20 ml. isobutyl alcohol 39 ml. water 1 ml. ammonia (25%)	As preceding
G	As above	Schleicher and Schull 589 (orange ribbon)

Curve *A* reported by A. E. F. Westman in a private communication.

Curves *B*, *C*, *E*, and *F* reported by E. Thilo *et al.*, *Sitzber. deut. Akad. Wiss. Berlin, Kl. Math. u. allgem. Naturw.*, **5**, 1 (1953).

Curves *D* and *G* reported by E. Karl-Kroupa[91] in *Anal. Chem.* Solvents previously described by J. P. Ebel *et al.*

ion might not pack well into a regular array with a given polyphosphate of moderate chain length so as to give a relatively stable lattice.

A third possibility is already within sight. This would be to use a continuous fractionation procedure which would lead to a clean separation between the various chain molecule-ions which have been demonstrated to exist in the vitreous phosphates. A procedure such as the continuous technique[107] in which descending-solvent chromatography is run at right angles

[107] See B. Sansoni and R. Klement, *Angew. Chem.*, **66**, 598 (1954) for application to condensed phosphates.

to electrophoresis could surely be improved to the point at which fractions amounting to several grams of the various chain phosphates might be isolated for detailed characterization.

KURROL'S AND MADDRELL'S SALTS

History of the Difficultly Soluble Crystalline Alkali Metal Metaphosphates

In 1833 Thomas Graham[37] gave a good description of the superficial properties and preparation of the insoluble sodium metaphosphate which is now commonly known as $NaPO_3$-II or Maddrell's salt. Probably this salt would be called "Graham's salt" except for the fact that this name was first applied to the vitreous sodium metaphosphate also described for the first time by Thomas Graham in the same publication. The name Maddrell's salt comes from two brief and somewhat discordant descriptions of a single experiment[108] carried out 14 years after Graham's work. Repetition of Maddrell's work gives a small yield of $NaPO_3$-II—the same material which is obtained when following the instructions given earlier by Graham.

$NaPO_3$-III, which is usually considered as the low-temperature variety of Maddrell's salt, was first described by Partridge, Hicks, and Smith,[4] who gave an incorrect x-ray pattern. The correct x-ray powder pattern appeared several years later.[109]

Another form of difficultly soluble sodium metaphosphate, $NaPO_3$-IV, is commonly called Kurrol's salt, since its discovery was attributed by Tammann[110] to his collaborator, Kurrol. The term Kurrol's salt is commonly used not only for $NaPO_3$-IV but for the difficulty soluble potassium metaphosphate, and sometimes it has been extended to cover all of the difficultly soluble alkali metal metaphosphates.

Perusal of the literature indicates that sodium Kurrol's salt is most readily formed by tempering a supercooled melt at about 550°C., whereas the Maddrell's salts ($NaPO_3$-II and -III) are usually made by dehydrating monosodium orthophosphate at temperatures below 475–500°C., as indicated in Table 10-1. The potassium Kurrol's salt is extremely easy to prepare,[12,24,38,39] in that it can be made by heating monopotassium orthophosphate to any temperature above about 150°C. (see Fig. 10-10). Both of the Kurrol's salts exhibit fibrous structures similar to asbestos, whereas the Maddrell's salts, made by relatively low temperature dehy-

[108] R. Maddrell, *Ann.*, **61**, 63 (1847); *Phil. Mag.*, **30**, 322 (1847).

[109] *ASTM Card Index of X-ray Diffraction Data, First Supplementary Set*, II—1725 (1945); also see ref. 10.

[110] G. Tammann, *J. prakt. Chem.*, **45**, 417 (1892).

dration of monosodium orthophosphate, are usually so finely crystalline that their cleavage and crystal habit cannot be observed visually. The classification of difficultly soluble metaphosphates into these two classes has also been made[111] on the basis that (1) Maddrell's salts are negligibly soluble in water and saline solutions at room temperature and (2) Kurrol's salts are negligibly soluble in water but are readily soluble in solutions of salts having other alkali metal cations. It should be noted that insoluble lithium and ammonium metaphosphates have also occasionally been described in the literature.[110,112]

Preparation of the Difficultly Soluble Alkali Metal Metaphosphates

As has been previously mentioned, the preparation of potassium Kurrol's salt is a very simple and straightforward process.[12,24,38,39] The rate of dehydration of potassium dihydrogen orthophosphate becomes appreciably fast around 205–208°C. Thermal analysis has shown that at about 258°C. a strong endothermic process takes place, during which water is lost very rapidly and the material froths. Also, it has been found that dipotassium dihydrogen pyrophosphate starts to decompose to form the potassium Kurrol's salt at temperatures around 150°C., and that at 230°C. the rate of formation of the potassium Kurrol's salt from the acid pyrophosphate is extremely rapid. Because of its rapid conversion to potassium Kurrol's salt, there is not a large build-up of $K_2H_2P_2O_7$ upon dehydrating potassium orthophosphates, such as is found when sodium orthophosphates are dehydrated. This does not mean, however, that the crystals of potassium Kurrol's salt form directly from the monopotassium orthophosphate upon heating. Rather, this process appears to be relatively complicated in that there is some build-up of intermediate phosphates.[39] In Figure 10-23, the course of dehydration of a sample heated in a furnace kept at 245°C. is shown. Unfortunately, the analyses given in this figure were obtained by wet-chemical methods and hence are not very precise; however, they do show that the dehydration is not a simple process in which one crystal is directly formed from another.

Although a number of different authors have given detailed instructions for making sodium Kurrol's salt, its preparation is still a capricious matter, and individual preparations often cannot be repeated. The most general

[111] P. Pascal, *Bull. soc. chim. France*, **35**, 1119 (1924). The idea of this author is brought up to date in the statement given herein.

[112] T. Fleitmann, *Ann. Physik*, **78**, 233, 338 (1849); A. Glatzel, *Inaugural Dissertation*, University of Wurzburg, Wurzburg, Germany, 1880, p. 28.

procedure for making sodium Kurrol's salt is to cool a sodium phosphate melt to temperatures in the range of 550–600°C. The surface of the melt can then be seeded to induce crystallization. A large number of seeding materials have been suggested. It is usually agreed that crystallites of Kurrol's salt itself, which were well washed to remove sodium trimetaphosphate, are very effective nuclei. However, silica, silicon carbide,

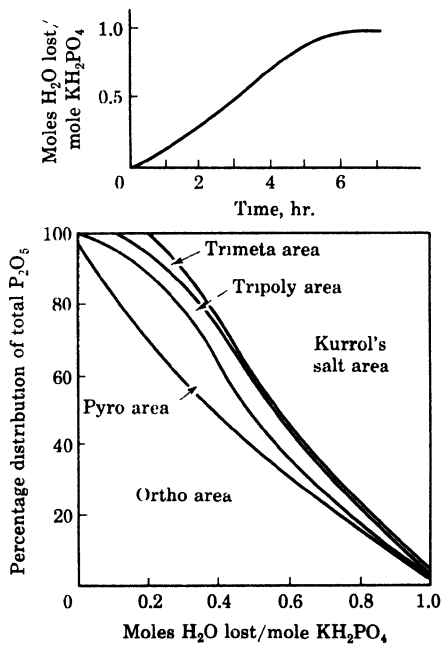


Fig. 10-23. The process of dehydration of monopotassium orthophosphate to potassium Kurrol's salt at 245°C.

potassium Kurrol's salt, and either of the forms of Maddrell's salt have been found to promote crystallization of the sodium Kurrol's salt.[113,114] When this is done, yields of sodium Kurrol's salt in the range of 50–90% of the total $NaPO_3$ can be obtained. In preparations made at the Monsanto laboratories, the fibrous crystals of Kurrol's salt are usually found in the center of the platinum dish in which the preparation was made, with sodium trimetaphosphate appearing above and below the crystals of Kur-

[113] B. Topley, *Quart. Rev.*, **3**, 345 (1949).

[114] H. Huber and K. Klumpner, *Z. anorg. u. allgem. Chem.*, **251**, 213 (1943).

rol's salt and sometimes completely surrounding the Kurrol's salt. A peculiar observation is that the seed crystals appeared to stay on top of the melt and were thus isolated from the region in which the crystal of Kurrol's salt eventually formed. However, if seeding is not used, only a very small proportion of Kurrol's salt is found in preparations made under otherwise apparently identical conditions.

It has been noted that Kurrol's salt is more readily obtained if the Na_2O/P_2O_5 mole ratio is a little higher[113] or lower[114] than unity. By seeding a melt in the temperature range of 580–590°C. and then tempering for 70–90 min. at 560–570°C., after which the crucible is rapidly cooled under flowing water, Thilo *et al.*[115] obtain plate-like crystals of sodium Kurrol's salt in 90–95% yield. He also reports small amounts of trimetaphosphate on the surface of the melt. The plate-like form of sodium Kurrol's salt described by Thilo appears to be a somewhat different modification from the usual fibrous form into which the plates convert upon being treated with water or left standing in the moist air.

In the dehydration of monosodium orthophosphate (see Table 10-1), sodium acid pyrophosphate is the first material to form; there seems to be a direct conversion from the crystalline orthophosphate to the crystalline pyrophosphate with the formation of little or no amorphous matter. In the temperature range of 260–335°C., there is a slow conversion of the crystalline $Na_2H_2P_2O_7$ to $NaPO_2$-II in the presence of water vapor. This rate becomes quite fast at 350°C. Form II of sodium metaphosphate is readily made in quite pure form by heating monosodium orthophosphate at 400°C. in the presence of steam. On the other hand, Form III is best prepared by heating monosodium orthophosphate in a dry atmosphere at 260°C. to give only partial conversion of the $Na_2H_2P_2O_7$ to the metaphosphate and then washing out the excess pyrophosphate with water.[116]

The exact conditions of heating are very important in making the various forms of sodium metaphosphate[10]—especially Form III. Water catalyzes the transitions, probably by plasticizing the amorphous-phase intermediates; and the Ostwald–Gay Lussac Step Rule plays an important role. This is exemplified by the fact[116] that at 275°C., extremely rapid heating of NaH_2PO_4 so as to cause it to melt in its water of composition during the conversion gives $NaPO_3$-I as the major constituent, slow heating in a humid atmosphere gives predominantly $NaPO_3$-II, and slow heating

[115] E. Thilo, G. Schulz, and E. M. Wichmann, *Z. anorg. u. allgem. Chem.*, **272**, 182 (1953).

[116] T. P. Kichline, L. R. Watson, and N. E. Stahlheber, private communication from the Monsanto Chemical Co.

in a very dry atmosphere (thin layer to avoid humidity build-up in the solid bed) gives $NaPO_3$-III in relatively large amounts.

In an attempt to grow sodium Kurrol's salt from P_2O_5-rich melts[114] made from 15 parts by weight of $NH_4H_2PO_4$ and 85 parts of NaH_2PO_4, following the usual procedure for obtaining sodium Kurrol's salt, mixtures of glass and the high-temperature form of Maddrell's salt ($NaPO_3$-II) were obtained. In this case,[87] the $NaPO_3$-II was in the form of transparent, acicular crystals several millimeters long which grew in spherical clumps. These large crystals of $NaPO_3$-II exhibit exactly the same x-ray powder pattern as the usual cryptocrystalline material. The crystals show parallel cleavage almost identical to that of the Kurrol's salts, and, on grinding in a mortar, they are reduced to a pulp of tiny fibers, as are the Kurrol's salts.

Dissolution and Precipitation of Maddrell's and Kurrol's Salts

The two varieties of Maddrell's salt, $NaPO_3$-II and $NaPO_3$-III are for all practical purposes insoluble in water, since their rate of dissolution is extremely slow. Thus at 25°C., Form II dissolves at a rate of 1.8×10^{-2} %/hr., when finely powdered, whereas Form III dissolves more rapidly, 0.34 %/hr. under the same conditions.[116] Both $NaPO_3$-II and $NaPO_3$-III dissolve at a much higher rate in salt solutions based on the ammonium or substituted ammonium ions or alkali metal ions other than sodium. Again, Form III seems to dissolve more rapidly than Form II under the same conditions.[116,113] In a solution of lithium chloride—which is especially efficacious in promoting dissolution—Form II dissolves at the rate of 33 %/hr. (25°C. and a Li/P mole ratio of 1.25) and Form III is all dissolved in a few minutes. Because the rate of dissolution of the Maddrell's salts in pure water is of the same order of magnitude as the rate of hydrolysis of chain phosphates, considerable hydrolysis is to be expected. This is found, since paper chromatograms of the solutions show short chains and rings. However, paper chromatograms of solutions made in aqueous lithium chloride show all nonmoving phosphates (chains or rings exhibiting more than about 10 phosphorus atoms).

$NaPO_2$-IV appears to be somewhat soluble in pure water since, after some days in cold distilled water and after a few hours in hot water, the fibrous crystals swell and become gummy. Eventually they dissolve entirely to give a highly viscous solution. As is the case with the Maddrell's salts, dissolution of sodium Kurrol's salt is greatly speeded up by the presence of salts having cations (especially Li^+) other than sodium which do not precipitate phosphates. Potassium Kurrol's salt behaves very

similarly to sodium Kurrol's salt, in that most preparations dissolve at a very slow rate in distilled water. However, some preparations appear to be more stable than others, since some finely ground asbestos-like fibers of potassium Kurrol's salt have shown no sign of becoming gummy after standing for about a week in distilled water at room temperature. On the other hand, potassium Kurrol's salt dissolves very rapidly in dilute solutions of salts of singly charged cations other than potassium.

The literature concerned with the dissolution of the difficultly soluble alkali metal metaphosphates indicates that the process of dissolution in solutions of simple salts containing cations other than the one appearing in the metaphosphate is an ion exchange process. It appears that dissolution of the long chains is effected by substitution of a different-sized ion in the crystal lattice of the difficultly soluble metaphosphate, so that the long chain anions in these salts are effectively "pried out" of the lattice. This process of dissolution can be extremely fast. Thus, when a finely ground sample of potassium Kurrol's salt having an average chain length of about 500 phosphorus atoms is added to a 0.2 *N* solution of sodium chloride which is being stirred violently in a Waring Blendor, a 1–5% viscous solution (in which there are no obvious signs of density, inhomogeneities, or undissolved particles) can be produced within several seconds after addition of the phosphate. An interesting example of the ion exchange type of dissolution is found in mixtures of potassium Kurrol's salt with any of the crude insoluble sodium metaphosphates. These mixtures are found to dissolve at a reasonable, and continuously accelerating, rate in distilled water under conditions when either of the insoluble materials will not dissolve by themselves. Apparently small amounts of the soluble phosphates which are present initiate the process by acting on the insoluble phosphate having the other cation.

An *excess* of singly charged cations other than the one appearing in the insoluble metaphosphate or the low molecular weight quaternary ammonium ions causes the formation of a gelatinous mass instead of a viscous solution. Likewise, the viscous solutions made by dissolving these phosphates in dilute salt solutions can be caused to precipitate a highly viscous, rather rubbery mass by adding additional salt or by adding organic materials soluble in water, such as alcohol or acetone. As might be expected, this salting out is a function of the chain length of the dissolved phosphate and also depends on the exact nature of the salting-out agent. By using relatively insoluble metaphosphates having high molecular weight anions, very rubbery masses can be prepared by alternately kneading and then washing the amorphous precipitate with a concentrated salt solution or an organic

material, such as alcohol or acetone. Although the salting-out process has not been carefully studied, Malmgren[8] has shown that for a given sample of potassium Kurrol's salt at 20°C., concentrations at which precipitation begins are 0.42 *N* for NaCNS, 0.90 *N* for Na_2SO_4, and 0.72 *N* for $Na_3P_3O_9$, whereas a saturated solution of $Na_4P_2O_7$ (0.82 *N*) does not salt out the metaphosphate.

Discussions of "double salt formation" which appear in the very early literature on the condensed phosphates gave proximate analyses of these amorphous precipitates. It appears that various amounts of different cations can be found in the precipitates, depending on the composition of the solution from which the precipitate was formed. Thus, the action of different concentrations of ammonium chloride for various lengths of time (with the ammonium chloride concentration being great enough to cause precipitation of the phosphate) on potassium Kurrol's salt can give a whole series of "mixed salts" varying from a relatively pure amorphous potassium phosphate to a relatively pure amorphous ammonium phosphate. A century ago it was believed that these amorphous compositions gave information as to the structure of the anion.

Multiply charged and heavy-metal cations give amorphous precipitates in the form of flocculent solids, rather than as high-viscosity fluids. An

TABLE 10-6
Precipitating Action of Various Cations on a Kurrol's Salt Solution

Cation	Required to form permanent precipitates: Ml. 0.1 *N* nitrate solution per 20 ml. Kurrol's solution	Equivalent of cation per mole of $NaPO_3$, ϵ	Radius of cation, *r* (A.)	ϵr^2
Ag^+	20 5	0 896	1 12	1 12
Sr^{2+}	16 4	0 701	1 27	1 13
Pb^{2+}	13 6	0 585	1.35	1 07
Ba^{2+}	12 6	0 540	1 45	1 10
Bi^{2+}	9 4	0 407	?	—

Note: Large cations (Ba^{2+}, Sr^{2+}, Pb^{2+}, Ag^+, Bi^{2+}, ZrO^{2+}, UO_2^{2+}, and Hg_2^{2+}) in excess give flocculent, solid precipitates, whereas smaller cations for which $r < 1.1$ A. (Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Hg^{2+}, and Cu^{2+}) give gummy or oily precipitates or turbidity.[116] The tetramethylammonium ion does not give a precipitate even at high concentrations.[116]

interesting study by Thilo[115,117] indicates that the amount of various nitrates required to produce a barely permanent precipitate with a given sample of sodium Kurrol's salt is dependent on the size of the cation, as shown in Table 10-6. Undoubtedly, the larger the size of the ion (and probably the greater its charge), the less of the ion is needed to form a precipitate with a phosphate of a given molecular weight. Conversely, the higher the molecular weight of the phosphate, the less of the salting-out agent is needed to form a precipitate.

Molecular Structure of Maddrell's and Kurrol's Salts

The most complete x-ray diffraction study on a difficultly soluble alkali metal metaphosphate has been done[118] on rubidium Kurrol's salt, $(RbPO_3)_n$. This structure consists of continuous P -O -P— chains, running in the direction of the fibrous cleavage and consisting of interconnected PO_4 groups. Each unit cell contains a portion of two different chains which spiral in opposite ways around the screw axes of the crystal, the pattern repeating itself every two phosphorus atoms in the chain, as shown in Figure 10-24. Thus, there are four units of $RbPO_3$ per unit cell. The P-O distances within the chain are 1.62 ± 0.03 A., and the distance between a phosphorus and either one of its pair of isolated oxygen atoms is 1.46 ± 0.05 A. This corresponds to 0.2 π-bond per σ-bond in the chain and 0.9 π-bond per σ-bond leading from the phosphorus to the oxygen atoms not in the chain, so that the over-all amount of 2π-bonds per phosphorus is unevenly distributed, with the least amount of π-character being in the chain-forming bonds. The O- P O angle between the two isolated oxygen atoms is large (123°) compared to the angle between oxygen atoms in the chain (99.5°). The P- -O -P bond angle in the chain is 129°.

It is interesting to note that all of the Kurrol's salts are monoclinic, with two sodium, the rubidium, and the cesium salts exhibiting a $P2_1/n$ space group and the potassium and calcium salts having a $P2_1/a$ space group. The rubidium and cesium salts are isomorphous. It appears that the chains in the cesium and perhaps in the well-known potassium Kurrol's salt exhibit the same configuration as was found for the rubidium salt described above. A preliminary study of one of the forms of sodium Kurrol's

[117] For further, more theoretical data on salting-out of phosphates, see U. P. Strauss, D. Woodside, and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).

[118] D. E. C. Corbridge, *Acta Cryst.*, **9**, 308 (1956), *ibid.*, **8**, 520 (1955); K. Pleith and C. Wurstner, *Z. anorg. u. allgem. Chem.*, **267**, 49 (1951); K. Born-Dornberger, *Angew Chem.*, **67**, 408 (1955).

salt suggests that the chains repeat every four phosphorus atoms instead of every two, as was found for the rubidium salt.

An x-ray structure study has been carried out[119] on the high-temperature form of Maddrell's salt, $NaPO_3$-II or insoluble metaphosphate. According to this work, the Maddrell's salt ($NaPO_3$-II) also consists of long —P—O—P— chains made up of interconnected PO_4 groups. However, the pattern of the chain repeats itself every three units as shown in Figure 10-24, and

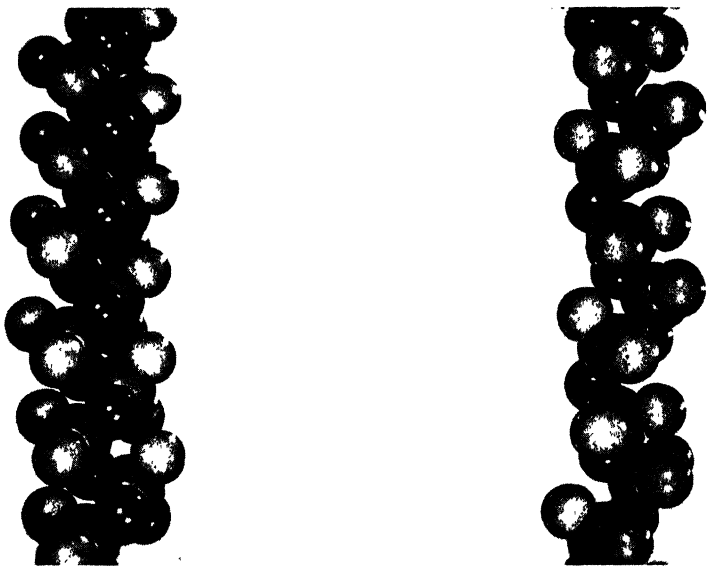


Fig 10-24. Portions of the metaphosphate chains running through (A) crystalline rubidium Kurrol's salt and (B) the high-temperature form of Maddrell's salt ($NaPO_3$-II).

the chain does not spiral. The structure, which is very close to that[120] of β-wollastonite, $CaSiO_3$, can be thought of in terms of a repeating unit of two PO_4 tetrahedra in line with the third tetrahedron placed out of line. The relative placement of the chains in the crystal has been suggested.[119]

The most careful studies of the molecular constitution of solutions of the difficultly soluble alkali metal metaphosphates have been carried out on potassium Kurrol's salt, probably because of the ease with which this

[119] K. Dornberger-Schiff, F. Liebau, and E. Thilo, *Acta Cryst.*, **8**, 752 (1955); E. Thilo, *Chem. Technik*, **4**, 343 (1952).

[120] M. J. Buerger, *Proc. Natl. Acad. Sci.*, **42**, 113 (1956).

material can be prepared and dissolved. A series of papers from Sweden[8,121] report a variety of physical-chemical studies on solutions of potassium Kurrol's salts. These studies include measurements by (a) the ultracentrifuge, (b) dialysis, (c) electrophoresis, and (d) dilute solution viscosity in the presence of swamping electrolytes. From this work it was found that the degree of polymerization of Kurrol's salt depended on the temperature of preparation and the length of time the sample was heated, as shown in Table 10-7.

TABLE 10-7

Physical Data on Solutions of Kurrol's Salt Prepared by Heating KH_2PO_4 for Various Periods at Various Temperatures[8, 121]

Temperature of preparation (°C)	Time at temperature (hr.)	Viscosity,[a] in salt solution (centipoises)	Sedimentation constant, S_0[b] (Svedberg units)	Diffusion constant, D[b] (10 c.g.s. units)	Degree of polymerization, $\bar{n}$, from equation[c] (zeta average[122])
260	215–280	1.53	10	1.7	2,300
290	120–280	1.93	14	1.4	3,900
305	140–190	3.47	26	1.5	6,700
382		3.47	27	1.0	9,300
445	0.5	2.51			
445	2.0	3.09			
445	4.0	3.36			
445	20	4.36			
445	115–240	4.60	25	0.6	11,700
495		2.60	34	1.2	11,000
665	30–200	4.22	30	0.6	19,500

[a] Measurements made on solutions prepared by dissolving 2.36 g. of potassium Kurrol's salt per liter of solution containing 10.2 g. of sodium trimetaphosphate

[b] Sedimentation and diffusion were studied in a 0.4 M sodium thiocyanate solution.

[c] $M = \frac{s}{D} \cdot \frac{RT}{1 - V\rho}$

As can be seen from Table 10-7, the molecular weights of these samples are extremely high, being in the range of 250,000 to several million. Similar data are presented in Table 8-8 on page 475. As this latter table dem-

[121] O. Lamm and H. Malmgren, *Z. anorg. u. allgem. Chem.*, **245**, 103 (1940); H. Malmgren and O. Lamm, *ibid.*, **252**, 256 (1944); H. Malmgren, *Acta Chem. Scand.*, **3**, 1331 (1949).

[122] International Union of Pure and Applied Chemistry, Commission on Macromolecules, Subcommission on Nomenclature: *J. Polymer Sci.*, **8**, 257 (1952)

onstrates, the molecular weights determined by the ultracentrifuge are somewhat dependent on the type and concentration of swamping electrolytes. However, the variation is relatively small—being approximately a factor of 2. Although the variation in the calculated degree of polymerization might be attributable to a changing amount of aggregation, it is believed that the effect is probably an artifact introduced by ignoring or imperfectly treating charge interactions in the mathematical interpretation of the data. Present-day studies are unearthing similar anomalies in studies of ionized organic macromolecules which definitely do not change their degree of polymerization and are not believed to form aggregates.

As described above, the application of the techniques of polymer physics to solutions of potassium Kurrol's salt shows that these materials have extremely high molecular weights. Now the question is whether these are long straight chains—since the metaphosphate composition is a limiting case for the polyphosphates—or whether they are structures containing a considerable number of branching points—since the metaphosphate composition is also a limiting case for certain ultraphosphates. Investigation of the shape of these molecule-ions by flow birefringence,[123] anisotropy in electrical conductivity,[124] and interpretation of sedimentation and diffusion data in terms of a shape factor,[8] all indicate that the molecule-ions are extended rods in aqueous solution which tend to coil up and become less asymmetric on the addition of a swamping electrolyte. Calculation[123] of a chain length from the rotary diffusion constant obtained by flow birefringence agrees quite well with the chain length obtained by intrinsic viscosity. Furthermore, chain lengths obtained from end-group titrations, on the assumption of long straight chains having weakly acidic hydrogens only at the ends, agree reasonably well with the degrees of polymerization obtained by other techniques.

All of this information leads to the conclusion that the usual potassium Kurrol's salt made by dehydrating monopotassium orthophosphate is a straight chain polyphosphate of a high degree of polymerization. As previously noted, polymerizations ranging from several hundred to several million phosphorus atoms per chain can be obtained by varying the heat treatment of the monopotassium orthophosphate, with higher temperatures and longer heating times resulting in longer chains. As is the case for so many crystalline organic high polymers, the crystal structure is not affected by very large changes in the molecular weight. This is because the individual chains pass through a large number of unit cells and probably terminate at crystal defects and junctures between microcrystallites. For a

[123] J. R. Van Wazer, M. Goldstein, and E. Farber, *J. Am. Chem. Soc.*, **75**, 1563 (1953).
[124] U. Schindewolf, *Z. physik. Chem., Neue Folge*, **1**, 9 (1954); *Naturwiss.* **16**, 435

potassium Kurrol's salt having a molecular weight of 2×10^6, a value which is at the upper end of the observed range, an average chain will pass through 10^4 unit cells in a crystal! The ultracentrifuge measurements indicate that there is a distribution of molecular sizes, but that the distribution is unusually sharp, as compared to reorganizing systems involving high polymers.

By varying the K_2O/P_2O_5 mole ratio from values considerably below to values considerably above unity, it is possible to produce a series of potassium Kurrol's salts,[125–127] the properties of which point up the chain structure of the Kurrol's salts made by dehydrating potassium orthophosphates for which K_2O/P_2O_5 equals unity. When a potassium orthophosphate mixture containing more than one mole of K_2O to each mole of P_2O_5 is dehydrated, the resulting Kurrol's salt is very similar to the Kurrol's salt made from an orthophosphate for which $K_2O/P_2O_5 = 1$, since the excess potassium remains in the liquid phase and later crystallizes out as $K_5P_3O_{10}$. The viscosity of a salt-free solution of the crude Kurrol's salt formed from a potassium-rich melt decreases with increasing potassium content but this is due to the tripolyphosphate's acting as an added low molecular weight electrolyte to cause coiling of the chains. When the $K_5P_3O_{10}$ is washed out of the crushed crude preparation with distilled water, the viscosity of the potassium Kurrol's salt (dissolved by use of an ion exchange resin) becomes relatively independent of the amount of K_2O in excess of $K_2O/P_2O_5 = 1$ in the original melt. However, for Kurrol's salt preparations made from melts deficient in K_2O, there appears to be crosslinking in freshly prepared solutions. This is demonstrated by a number of different experiments.

The viscosity of salt-free solutions of the crude Kurrol's salt preparations which were dissolved by mixing with Graham's salt ($NaPO_3$ glass), are shown as a function of the K_2O/P_2O_5 mole ratio in Figure 10-25. It is seen that the viscosity measured at a 0.2% concentration of the crude Kurrol's salt goes through a maximum at K_2O/P_2O_5 = about 0.9. This effect is attributed to crosslinking in those samples of potassium Kurrol's salt for which K_2O/P_2O_5 is less than unity. The drop in viscosity for

[125] R. Pfansteil and R. K. Iler, *J. Am. Chem. Soc.*, **74**, 6059 (1952).

[126] E. J. Griffith, private communication and information presented at the *Spring Meeting of the American Chemical Society in Cincinnati, Ohio, April 7, 1955, before the Division of Physical and Inorganic Chemistry.*

[127] W. Dewald and H. Schmidt, *J. prakt. Chem.*, **44**, 196 (1955).

K_2O/P_2O_5 ratios greater than unity is attributed to coiling of the chains because of the presence of $K_5P_3O_{10}$.

Added proof that there is crosslinking in these ultraphosphate samples is given by the change in viscosity with time. After keeping a sample of potassium Kurrol's salt for which $K_2O/P_2O_5 = 0.99$ and another sample for which $K_2O/P_2O_5 = 1.01$ for one day or longer at pH 8 and 25°C., the viscosity numbers are approximately the same. However, the viscosity

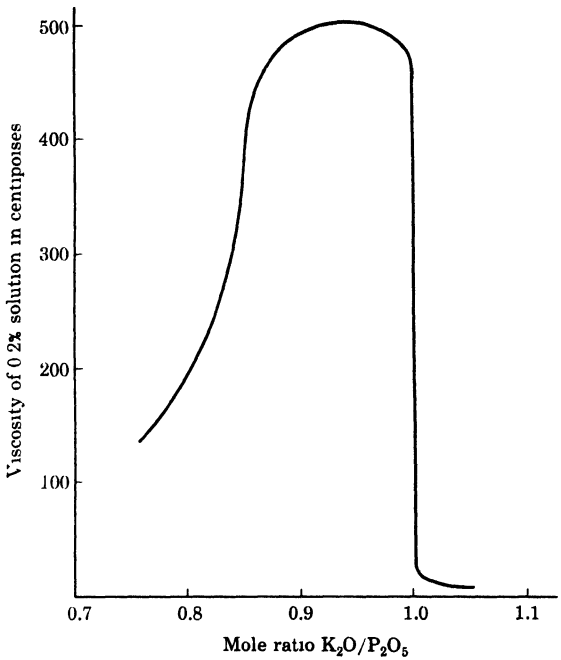


Fig. 10-25. Viscosity of salt-free solutions freshly prepared from potassium Kurrol's salts exhibiting different K_2O/P_2O_5 ratios.

number of freshly prepared solution of the Kurrol's salt for which $K_2O/P_2O_5 = 0.99$ is more than ten times higher (at 1% concentration) than the viscosity number of the freshly prepared material having $K_2O/P_2O_5 = 1.01$. This unusually rapid hydrolysis indicates the presence of branching points in the potassium Kurrol's salt having a deficiency of K_2O. The crosslinked Kurrol's salts will be discussed in greater detail under ultraphosphates in Chapter 12.

Because of the preliminary data obtained by x-ray analysis[119] and from

the small amount of work that has been done on its flow birefringence[121] and hydrolysis,[119] it appears that sodium Kurrol's salt contains long, straight chain molecule-ions as does potassium Kurrol's salt.

The high viscosity obtained upon dissolving the high-temperature form of Maddrell's salt ($NaPO_3$-II) indicates a high molecular weight structure for the phosphate molecule-ions in agreement with the x-ray diffraction data. Although the various physical techniques of the solution chemistry of polymers have not been applied to determining the structure of Maddrell's salt, Thilo[128] has interpreted some purely chemical data as a proof of the structure of this material. In this work, Thilo made a series of mixed metaarsenatophosphates of which the limiting member on the phosphate side was the high-temperature Maddrell's salt ($NaPO_3$-II). As demonstrated by x-ray diffraction powder diagrams, the crystal structure of the arsenatophosphates appears to be quite similar to the Maddrell's salt. A plot of density *versus* per cent P_2O_5 and monomeric molecular volume *versus* per cent P_2O_5 indicated that, for $4 > As_2O_5/P_2O_5$ mole ratio, there is a linear decrease with per cent P_2O_5, and that these linear curves extrapolated in both cases to the measured density or volume for $NaPO_3$-II. As is generally known, the As—O—As and As—O—P bonds hydrolyze immediately upon dissolution of the substance in water, whereas P—O—P bonds not at branching points are extremely stable. Upon dissolving the various metaarsenatophosphates, it was found that all of the arsenic was present in the form of orthoarsenate, and the phosphate appeared as short chains of various lengths. It was then concluded that the arsenatophosphates had long chains in their solid structure, and that this was also the structure of the pure phosphate, Maddrell's salt.

The only structure in the series of metaphosphates known as Maddrell's and Kurrol's salts which has not been shown to be a long chain by some more-or-less acceptable proof is the low-temperature form of Maddrell's salt ($NaPO_3$-III). However, solutions of this material exhibit a relatively high viscosity, which would imply that reasonably high molecular weight chains are present. Because of the difficulty in dissolving both forms of Maddrell's salt, the possibility that these materials might represent rings connected together by long, straight chain segments should not yet be completely discounted. Such hypothetical limiting ultraphosphates are discussed in Chapter 11.

[128] E. Thilo and L. Kolditz, *Z. anorg. u. allgem. Chem.*, **278**, 122 (1955); E. Thilo and I. Plaetschke, *Z. anorg. Chem*, **260**, 297 (1949).

CHAPTER 11

Ring and Branched Phosphates

HISTORY

The salt which we now know as sodium trimetaphosphate was prepared by Fleitmann and Henneberg,[1] who, on the basis of structure proofs which would be completely unacceptable today, called the material a trimetaphosphate. The present-day cyclic formulation of its structure was first proposed by Lindbom in 1875.[2] The salt which is now known as sodium tetrametaphosphate was first prepared[3] by Fleitmann and given its present-day name by Tammann.[4] The modern cyclic formulation of the tetrametaphosphate anion was suggested by Glatzel.[5]

For many decades after the discovery of the sodium trimeta- and tetrametaphosphates, controversy raged in the scientific literature as to the degree of polymerization of these salts. Thus, the trimetaphosphate was also known as a monometa- and dimetaphosphate, with these latter names stemming from misinterpretation of colligative measurements. In the late 19th and early 20th centuries, a large number of impure preparations which contained high proportions of ring phosphates were made and assigned various degrees of polymerization[6] as metaphosphates by the use of various techniques of classical physical chemistry. The stumbling block in all of this work was that the experimenter did not know the degree of dissociation of the cations in the various preparations when studied in aqueous solution under different experimental conditions. The first definite proof of ring structure in one of these compounds came from an x-ray study.[7]

[1] T. Fleitmann and W. Henneberg, *Ann. Chem.*, **65**, 304 (1848).

[2] C. G. Lindbom, *Ber.*, **8**, 122 (1875).

[3] T. Fleitmann, *Ann Chem.*, **72**, 228 (1849).

[4] G. Tammann, *Z. phys. Chem.*, **6**, 122 (1890); *J. prakt. Chem*, **45**, 417 (1892).

[5] A. Glatzel, "Ueber die Salze der Dimeta und Tetrametaphosphate," *Inaugural Dissertation*, Wurzburg, 1880.

[6] Some of these are reviewed by K. Karbe and G. Jander, *Kolloid-Beih.*, **54**, 1 (1943) and by D. M. Yost and H. Russell, *Systematic Inorganic Chemistry*, Prentice-Hall, Inc., New York, 1946, pp. 210–24.

[7] L. Pauling and J. Sherman, *Z. Krist.*, **96**, 481 (1937).

The earliest papers on phosphates containing more P_2O_5 than corresponds to the metaphosphate composition were written by Kroll,[8] who called these compounds ultraphosphates. Since the time of Kroll, there has been very little work on the ultraphosphates as compared to the voluminous literature concerned with materials having the metaphosphate composition.

GENERAL BEHAVIOR OF RING AND BRANCHED PHOSPHATES

Although most phosphates give precipitates with multiply charged and heavy metal ions, the ring compounds form relatively soluble salts with a number of metals. As might be expected, the alkali metal, ammonium, and substituted ammonium salts have high solubilities; but in addition, such compounds as the silver, calcium, and copper salts exhibit solubilities in the neighborhood of several grams per liter. The ring compounds are less strong complexing agents than the chain phosphates. In the lingo of technology, the ring phosphates are not "sequestering agents." In line with this, the ring acids are very strong and exhibit no weak hydrogens.

The ring phosphates, like the chain phosphates, are very stable in aqueous solution at neutral pH and room temperature. However, splitting of the rings so as to form chains occurs quite rapidly in strongly basic solutions in which the chain phosphates are relatively very stable. As is the case with all condensed phosphates, hydrolysis of the rings is catalyzed by hydrogen ions, so that there is rapid degradation in strongly acidic solutions.

Thus far only two ring phosphates, the trimeta- and tetrametaphosphates, have been isolated in large amounts. The trimetaphosphate has a six-membered ring of alternate phosphorus and oxygen atoms, and the tetrametaphosphate has an eight-membered ring. According to the theory of ring strain which has been developed for the cyclic hydrocarbons (the carbons in which exhibit about the same bond angles as the phosphorus and, to a poorer approximation, the oxygen atoms), these six- and eight-membered rings should be very stable and easy to make.[9] Larger rings should have a smaller probability for forming and may also be difficult to pack into crystals because the large chains are flexible and the units of the structure bear charges.

[8] A. V. Kroll, *Ueber Ultraphosphate*, Leipzig, 1912; *Z. anorg. Chem.*, **76**, 387 (1912); *ibid.*, **77**, 1 (1912); **78**, 95 (1912); *J. Iron Steel Inst. (London)*, **84**, No. 2, 126 (1911); *Stahl u. Eisen*, **28**, 675 (1908); and *ibid.*, **31**, 2020 (1911).

[9] L. Ruzicka, *Chemistry & Industry*, **54**, 2 (1935); and G. W. Wheland, *Advanced Organic Chemistry*, 2nd ed., John Wiley & Sons, Inc., N. Y., 1949.

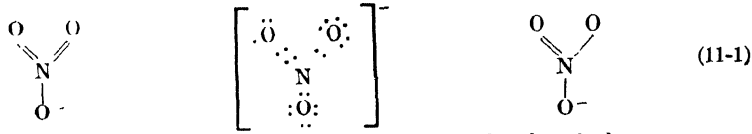
The ultraphosphates generally decompose upon dissolution in water. With the exception of a few simple fused-ring compounds, such as the P_4O_{10} molecule, the ultraphosphates should be slowly soluble, and this has been the case with the few ultraphosphates which have been prepared and studied. As was previously pointed out in Chapter 8, the lower molecular weight ultraphosphate compounds must exhibit values of the M_2O/P_2O_5 mole ratio in which both the numerator and denominator are small whole numbers.

RING PHOSPHATES

Monometa- and Dimetaphosphates

Although both monometa- and dimetaphosphates have been described in the literature, neither of them has been proven to exist. Since it could not possibly exhibit sp^3-hybridization of the phosphorus, a monometaphosphate is not to be expected. However, dimetaphosphates can probably be prepared by low-temperature synthesis.[10]

The only way to formulate a monometaphosphate is to use sp^2-hybridization of the phosphorus with π-bonding. Such a structure would be identical to that of the planar nitrate ion depicted below:



classical valence-bond notation | electronic representation (a resonance form) | bond equivalent of electronic representation (11-1)

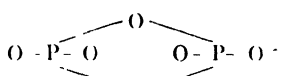
The sp^2-type of hybridization does not appear below the first row in Groups IV and V of the periodic table, since the additional stabilizing energy due to π-bonding can be achieved by using d-electrons in the π-bond orbitals rather than p-electrons. Thus, although the carbonate and nitrate ions exhibit planar symmetry with a three-fold axis perpendicular to the plane, silicate and phosphate ions have tetrahedral symmetry. It follows that carbonates and nitrates are found only as mononuclear ions, whereas the equivalent oxyacids of the heavier elements in Groups IV and V can form polynuclear molecule-ions of complicated structure.

A number of the incorrectly named monometa- and dimetaphosphates

[10] J. R. Van Wazer and E. J. Griffith, *J. Am. Chem. Soc.*, **77**, 6140 (1955).

described in the literature were studied by Ebel,[11] who showed that they consisted of mixtures of known chain or ring phosphates. According to Ebel (and, in some cases, other modern workers), the monometaphosphate of Beans and Kiehl[12] and the sodium dimetaphosphate of Travers and Chu[13] really consist of the trimetaphosphate described in the following section. The dimetaphosphoric acid of Travers and Chu[14] is really a tetrametaphosphate. Furthermore, the monometaphosphate of Pascal,[15] as well as the dimetaphosphates of Pascal and Réchid[16] and of Bonneman-Bémia[17] all consist of mixtures, primarily of chain phosphates. The dimetaphosphate of Laforgue-Kantzer[18] is a mixture of low molecular weight known phosphates, containing a considerable amount of pyrophosphate. As late as 1944 some of this work on dimetaphosphates was included in a textbook[6] (published 1946) because of its supposed scientific interest.

A recent note[19] from a leading x-ray laboratory described an ammonium dimetaphosphate, $(NH_4)_2P_2O_6 \cdot 6\,H_2O$, in which the



structure was said to be indicated by a Patterson projection. This result, however, was promptly shown to be incorrect, since the same crystals which were used in the structure study proved to be an orthophosphate—microcosmic salt, $Na(NH_4)HPO_4 \cdot 4\,H_2O$. The assumed hexahydrate of ammonium dimetaphosphate would have had a molecular weight of 205 as compared to the molecular weight of 209 for microcosmic salt; and chemical analyses for ammonia and phosphorus are practically identical for both materials (8% of NH_3 and 39% of P_2O_5). The crystals were found to exhibit (1) the correct x-ray powder pattern for microcosmic salt, (2) the proper analysis for sodium, and (3) the optical and chemical properties of microcosmic salt under the microscope.

[11] J. P. Ebel, *Bull soc. chim. France*, **20**, 1089 (1953).

[12] H. T. Beans and S. J. Kiehl, *J. Am. Chem. Soc.*, **49**, 1878 (1927).

[13] A. Travers and Y. K. Chu, *C. R. Acad. Sci.*, **198**, 2100 (1934).

[14] A. Travers and Y. K Chu, *C. R. Acad. Sci.*, **198**, 2169 (1934).

[15] P. Pascal, *Bull. soc. chim.*, **1923**, 1611; *C. R. Acad. Sci.*, **176**, 1398 (1923).

[16] P Pascal and Mme. Réchid, *C. R. Acad. Sci.*, **196**, 828 (1933); Mme. Réchid, *C. R. Acad. Sci.*, **196**, 860 (1933).

[17] P. Bonneman-Bémia, *Ann. Chim.*, **16**, 395 (1941).

[18] D. Laforgue-Kantzer, Thèse Doct Sci. Phys., Paris, 1949.

[19] R. Pepinsky, C M McCarty, E Zemyan, and K. Drenck, *Phys. Rev.*, **86**, 793 (1952).

The conclusion from all of this is that as yet no one has made a dimetaphosphate; but there is no reason that such a salt cannot be prepared. However, it is expected that, when a soluble dimetaphosphate is made, it will hydrolyze very rapidly in water to give the pyrophosphate ion[10,11] and thus relieve the strain in the four-membered ring based on quadruply connected phosphorus.

Preparation of Trimetaphosphates

The parent compound from which nearly all other trimetaphosphates are prepared today is the sodium salt. This material, which has been manufactured on a commercial scale, is usually made by heating monosodium phosphate to temperatures between 500 and 600°C.,[20] allowing sufficient time (a few minutes at temperature) for loss of water of composition of the orthophosphate. The sodium trimetaphosphate forms very readily as a well-crystallized salt. It can also be prepared by cooling a sodium metaphosphate melt to the right temperature range or by heating various mixtures of sodium phosphates exhibiting an over-all composition corresponding to the metaphosphate. An interesting demonstration that this composition can be reached by various paths is found in one of the classical preparations[21,22] of sodium trimetaphosphate in which sodium pyrophosphate is treated with ammonium chloride according to the following equation:

$$3\ Na_4P_2O_7 + 6\ NH_4Cl \xrightarrow{\Delta} 2\ Na_3P_3O_9 + 6\ NaCl + 6\ NH_3 \uparrow + 3\ H_2O \uparrow \qquad (11\text{-}2)$$

Naturally, trimetaphosphate will not be the sole product in the above reaction unless the heat treatment allows its crystals to form to the exclusion of other metaphosphates.

Recent work[23] has shown that an acid sodium trimetaphosphate, $Na_2HP_3O_9$, can be prepared thermally by evaporating an aqueous orthophosphate liquor having an Na_2O/P_2O_5 mole ratio of $^2/_3$ and allowing crystallization to proceed at 300°C. when the H_2O/P_2O_5 mole ratio reaches the correct value of $^1/_2$. Proof that this material is a trimetaphosphate was obtained by chromatographic analysis and by the x-ray pattern of the neutral sodium salt made from it by adding sodium hydroxide to its aqueous solution. The acid salt, $Na_2HP_3O_9$, appears in the phase diagram of Figure 11-1.

[20] R. N. Bell, *Inorganic Syntheses*, ed. L. F. Audrieth, McGraw-Hill Book Co., New York, 1950, Vol. III, pp. 103-06, recommends 5 hr. at 530°C.

[21] A. Jamieson, *Ann Pharm*, **59**, 350 (1842)

[22] G. von Knorre, *Z. anorg. Chem*, **24**, 381 (1900).

[23] E. J. Griffith, *J. Am. Chem. Soc.*, **78**, 3867 (1956); *ibid.*, **76**, 5892 (1954).

Another recently discovered sodium trimetaphosphate[24] is the double salt $Na_9K_3(P_3O_9)_4$, shown in the phase diagram of Figure 10-3 (p. 609). This salt can be made thermally,[25] and it can also be prepared by precipitation from solution with methanol. Proof that it is a trimetaphosphate is obtained by removing the metal cations with an ion exchange resin and replacing them with sodium to give a salt which has all of the physical characteristics, including x-ray pattern, of sodium trimetaphosphate. Since

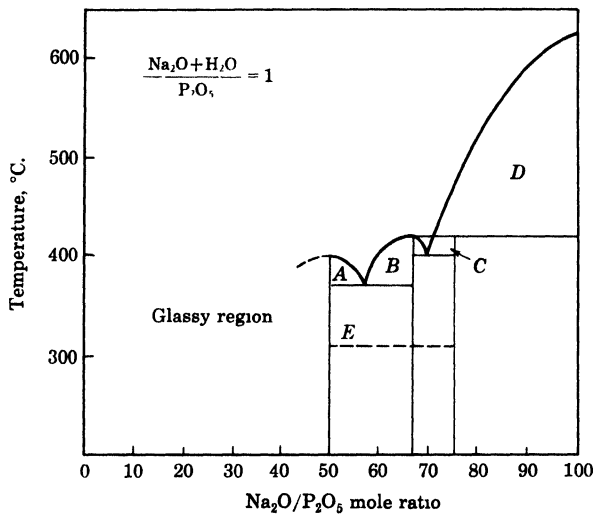


Fig. 11-1. Phase diagram of the sodium acid phosphate system. Area *A* contains $Na_2H_2P_4O_{12}$ plus liquid; area *B*, $Na_2HP_3O_9$ plus liquid, area *C*, $[Na_3H(PO_4)_4]_n$ plus liquid, and area *D* contains $Na_3P_3O_9$ plus liquid At *E* there is a transition between the cyclic $Na_2HP_3O_9$ and a water-insoluble isomer, $[Na_2H(PO_3)_3]_n$, stable below about 300°C.

there are three moles of sodium to one mole of potassium in this metaphosphate, the old idea of obtaining structural data from the composition of double salts would indicate incorrectly that this salt is a tetrametaphosphate.

As late as 1949, B. Topley in *Quart. Rev.*, **3**, 353 (1949), used the composition of double salts as part of the evidence supporting the trimeric formula of sodium trimetaphosphate. He said "Sodium trimetaphosphate ($NaPO_3$-I) forms a series of well-defined salts containing one atom of Na° and 1 of M°°, of which $NaBaP_3O_9 \cdot 4\ H_2O$ is typical. It was the discovery of these double salts that led Fleitmann and Henneberg to the conclusion that the soluble crystalline sodium metaphosphate which they obtained by slow cooling of a melt was trimeric."

[24] E. J. Griffith and J. R. Van Wazer, *J. Am. Chem. Soc.*, **77**, 4222 (1955).
[25] G. W. Morey, *J. Am. Chem. Soc.*, **76**, 4724 (1954).

The fact that the salt is really a trimetaphosphate shows that the composition of double salts has little or nothing to do with the structure of the anion.

Of all of the condensed phosphates, except perhaps the pyrophosphates, the most work on the preparation of various metal salts has been done with the trimetaphosphate ion. Most of this work was carried out before 1900, and a listing of the trimetaphosphates prepared by the more important workers[1,2,4,22,26,27] in the field is given in Table 11-1. It is believed that nearly all of the salts described in Table 11-1 correspond to well-crystallized compounds, since the high solubility of the multiply charged and heavy metal salts of the trimetaphosphate ion allows crystallization to proceed gradually. Most of the salts were made by mixing solutions of the sodium salt with a soluble salt of the multiply charged or heavy metal and then evaporating, so that the crystals grew gradually as the solution was concentrated. Unfortunately, some of the preparations of sodium trimetaphosphate used by the early workers were quite impure,[6] so that the resulting preparations were sometimes contaminated with phosphates other than the trimeta.

TABLE 11-1
Some Trimetaphosphates Described in the Literature

Salt	Reference	Salt	Reference
$Na_4Mg(P_3O_9)_2 \cdot 5\ H_2O$	2,23	$K_3P_3O_9$	2
$NaCaP_3O_9 \cdot 3\ H_2O$	2,23	$(NH_4)_3P_3O_9$	2
$NaSrP_3O_9 \cdot 3\ H_2O$	2,23	$Ag_3P_3O_9$	1
$NaBaP_3O_9$	1	$Ag_3P_3O_9 \cdot H_2O$	1,22
$NaBaP_3O_9 \cdot 4\ H_2O$	1	$Ag_3P_3O_9$ 13–15 H_2O (?)	2
$KBaP_3O_9 \cdot H_2O$	2,23		
$NH_4BaP_3O_9 \cdot H_2O$	2,23		
$Ca_3(P_3O_9)_2 \cdot 9\ H_2O$	28		
$Ba_3(P_3O_9)_2$	1	$Mn_3(P_3O_9)_2 \cdot 9$–$11\ H_2O$ (?)	4,22
		$Zn_3(P_3O_9)_2 \cdot 9\ H_2O$	4
$Na_2Ni_2(P_3O_9)_2 \cdot 9\ H_2O$	4	$Cu_3(P_3O_9)_2 \cdot 9\ H_2O$	4
$Na_4Ni(P_3O_9)_2 \cdot 8\ H_2O$	2,23	$Co_3(P_3O_9)_2\ 9\ H_2O$	4
$Na_4Co(P_3O_9)_2 \cdot 8\ H_2O$	2,23	$Fe_3(P_3O_9)_2 \cdot 12\ H_2O$	2
$Na_4Cd(P_3O_9)_2 \cdot 4\ H_2O$	23	$Pb_3(P_3O_9)_2 \cdot 3\ H_2O$	1

The ability to form double salts is so pronounced in the case of the trimetaphosphates that, even though a large excess of calcium chloride is added to a solution of sodium trimetaphosphate, only the sodium-calcium double

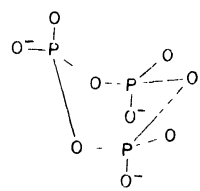
[26] A. Wiesler, *Z. anorg. Chem.*, **28**, 177 (1901).
[27] A. Boullé, *Compt. rend.*, **206**, 517 (1938).

salt is obtained.[27] The only completely substituted calcium salt described in Table 11-1 was prepared by Boullé,[27] who first made silver trimetaphosphate and then reacted it with calcium chloride. By evaporation of this solution under vacuum, he obtained large white crystals and, by precipitation with alcohol, a white powder—both exhibiting the composition $Ca(P_3O_9)_2 \cdot 9H_2O$. This compound, which was found to be crystalline to x-rays, loses about six moles of water at 110°C. with a complete collapse of the crystal lattice. At 350°C. the remaining water is lost, and an amorphous substance is formed, which, on heating for several hours, yields a very insoluble metaphosphate composition—presumably a mixture of chain anions.

Early preparations of the trimetaphosphoric acid as well as its highly soluble salts, such as the ammonium and potassium salts, were obtained[22] by such procedures as treating the lead salt reported in Table 11-1 with the respective sulfide (H_2S, K_2S, etc.). However, the modern way of making the acid and many of its salts is to remove the sodium from sodium trimetaphosphate by means of a cation exchange resin.[28] By this means, trimetaphosphates of lithium, potassium, ammonium, and tetramethylammonium ions have been prepared. The free acid has also been made in solution but so far has not been concentrated without considerable molecular reorganization, as shown chromatographically.

Proofs of the Trimetaphosphate Structure

The trimetaphosphate ion is a six-membered ring of alternate phosphorus and oxygen atoms, as shown below:



The proof for this structure rests on a considerable body of evidence which, when taken in its entirety, is quite convincing. This evidence is reported below:

1. An x-ray structure study[29] on the hexahydrate, $Na_3P_3O_9 \cdot 6\,H_2O$, shows that compound contains six-membered rings of alternate phosphorus

[28] J. R. Van Wazer and K. A. Holst, *J. Am Chem. Soc.*, **72**, 639 (1950); also various studies not reported in the literature.

[29] V. Caglioti, G. Giacomello, and E. Bianchi, *Atti. accad. Italia Rend.*, **3**, 761 (1942).

and oxygen atoms. However, the work was not carried to the point where oxygen-to-phosphorus distances could be determined. In the triclinic $Na_3P_3O_9 \cdot 6\ H_2O$ crystal there are two of these formula weights per unit cell. Another x-ray study[30]—this time on anhydrous $Na_3P_3O_9$—shows that the crystal symmetry is consistent with either a cyclic-trimeric or a monomeric metaphosphate (and the monomer is disallowed on other grounds, as described previously).

2. The nuclear magnetic resonance spectrum of phosphorus in solutions of sodium trimetaphosphate shows only the resonance peak corresponding to middle groups.[31] This information substantiates the ring formation of the structure, as does the fact that all of the hydrogens in trimetaphosphoric acid are strong and practically equivalent[32,33] to each other (see Fig. 11-3).

3. Careful measurements[33] of the conductance of dilute solutions of sodium trimetaphosphate and trimetaphosphoric acid show that these compounds dissociate into singly charged ions plus triply charged ions. This substantiates the trimeric formulation.

4. Molecular weight determinations[17] based on the freezing point lowering of sodium trimetaphosphate in sodium sulfate decahydrate gave values of 307-313, as compared to the theoretical value of 306 for $Na_3P_3O_9$. In water as a solvent, the molecular weight was found[34] to agree better with the supposition of a triply charged anion than with any alternative when approximate corrections were made for the effect of ionic strength upon the freezing point lowering.

5. The presence of three phosphorus atoms per ring is also indicated by the nearly quantitative hydrolysis of the trimetaphosphate ion to tripolyphosphate in alkaline solution.[35] Although hydrolysis data usually do not afford satisfactory structure proofs, the similar alkaline hydrolysis[36] of tetrametaphosphate ion (the structure of which has been elegantly established by x-ray diffraction) to tetrapolyphosphate lends creditability to the trimeric structure of the trimetaphosphate.

[30] B. Raistrick, *Lecture at the Canadian Institute of Chemistry, Halifax*, **1949**; B. Topley, *Quart. Rev.*, **3**, 353 (1949).

[31] J. R. Van Wazer, C. F. Callis, and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 4945 (1955).

[32] H Rudy and H. Schloesser, *Ber.*, **73**, 484 (1940); W. Treadwell and F. Leutwyler, *Helv. Chim. Acta*, **21**, 1450 (1938); also see ref. 29.

[33] C. W. Davies and C. B. Monk, *J. Chem. Soc.*, **1949**, 413.

[34] P. Nylen, *Z. anorg. u. allgem. Chem.*, **229**, 30 (1937).

[35] G. B. Hatch, U. S. Pat. 2,365,190 (1944, assigned to Hall Labs).

[36] For example, O. T. Quimby, *J. Phys. Chem.*, **58**, 603 (1954); also see A. E. R. Westman and A. E. Scott, *Nature*, **168**, 740 (1951).

6. Paper chromatography shows the trimetaphosphate ion to be a member of the same series of structures (rings) as the tetrametaphosphate and to be smaller than the tetrametaphosphate anion. It appears that boat and chair forms of the trimetaphosphate anion show up on the chromatograms.

Properties of Some Sodium Trimetaphosphates

There are three crystal forms of anhydrous sodium trimetaphosphate,[37] which are known as $NaPO_3$-I, $NaPO_3$-I′, and $NaPO_3$-I″. The phase relationships in the sodium metaphosphate system according to Liddell are

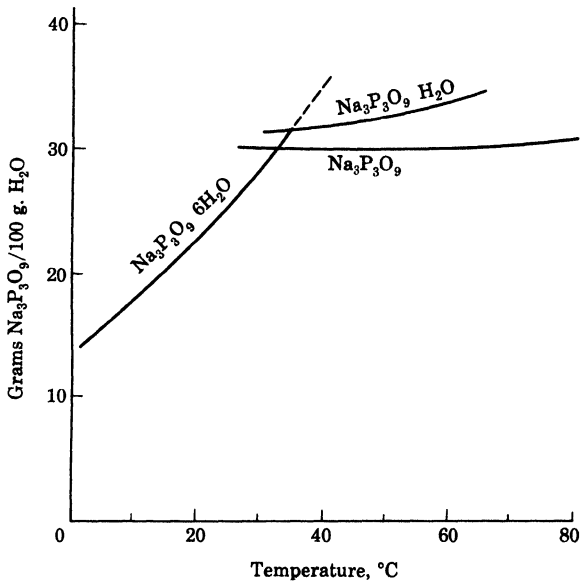


Fig. 11-2. Solubility of sodium trimetaphosphate in water as a function of temperature.

shown in Table 10-1 (Chapt. 10, p. 606). It is generally supposed that these three crystal forms dissolve to give identical solutions. Whether or not this is so, it is known that all three forms can be recrystallized from water as the hexahydrate or, above about 40°C., as the monohydrate.[30] An anhydrous form of $Na_3P_3O_9$ can be crystallized by holding the monohydrate in contact with its saturated solution at 60°C. for several days. This an-

[37] R. W. Liddell, *J. Am. Chem. Soc.*, **71**, 207 (1949).

hydrous form is shown to be identical with $NaPO_3$-I by x-ray diffraction. Form I is also said to be obtained by the nondestructive thermal dehydration of the various hydrates.

The hexahydrate and monohydrate of sodium trimetaphosphate are well known.[6,37] A recent study has shown that there are two forms of the monohydrate,[38] as well as a sesquihydrate and perhaps a hemihydrate. The usual way of preparing the hexahydrate is to evaporate a sodium trimetaphosphate solution at temperatures below about 25°C. The solubility of the hexahydrate is shown in Figure 11-2. Form I of the monohydrate is obtained by evaporating a very thin layer of solution at temperatures between 40 and 50°C. Precipitation with acetone at room temperature from very dilute solution also gives $Na_3P_3O_9 \cdot H_2O$-I. On the other hand, the form II of the monohydrate is obtained by precipitation with acetone from a concentrated solution at temperatures between 30 and 50°C. $Na_3P_3O_9 \cdot H_2O$-II can also be obtained by evaporation of a saturated solution at 60°C. and by dehydration of the hexahydrate at the same temperature in an atmosphere saturated with water. The sesquihydrate, $Na_3P_3O_9 \cdot 1.5\ H_2O$, is made by evaporation of a trimetaphosphate solution at 30°C. The crystals characteristically form on the walls of the container.

It is conceivable that the polymorphism of anhydrous sodium trimetaphosphate and its hydrates is attributable to different configurations (as in "boat" and "chair" forms) of the cyclic trimetaphosphate anion. This idea is now being investigated at Monsanto and Johns Hopkins University.

There is a great deal of metastability in the solubility relationships of the various hydrates of sodium trimetaphosphate. The solubility curves of the anhydrous salt and the monohydrate shown in Figure 11-2 exemplify this situation.[39] According to a schematic phase diagram given by Thilo and Wallis,[38] the hexahydrate is the stable crystalline phase in equilibrium with the saturated solution below about 30°C., the sesquihydrate is stable between about 30 and 40°C., and Form II of the monohydrate is stable between about 40 and 55°C., with the anhydrous salt being the stable form at higher temperatures. Form I of the monohydrate is metastable over the entire stability region of Form II of the monohydrate and can also be obtained at lower temperatures where the sesquihydrate is the stable form. Form II of the monohydrate, according to these authors, is metastable above 60°C. Depending on the concentration of the solution and the ex-

[38] E. Thilo and M. Wallis, *Chem. Ber.*, **9**, 1213 (1953); E. Thilo and U. Hauschild, *Z. anorg. Chem.*, **261**, 324 (1950).

[39] Private communication from B. Topley of Albright and Wilson, Ltd. (England) describing the work of J. E. Such and A. G. Taylor.

act procedure used in evaporating or salting out the crystals, several different hydrates can be obtained at the same temperature, either individually or as mixtures. It appears that additional work will be needed to clear up the question of which hydrate of sodium trimetaphosphate will form under a given set of circumstances.

The hexahydrate of sodium trimetaphosphate, as well as the sesquihydrate, can be dehydrated by heating without decomposition of the trimetaphosphate anion. However, in the case of both forms of the monohydrate, considerably decomposition occurs, so that as much as about 50% of the

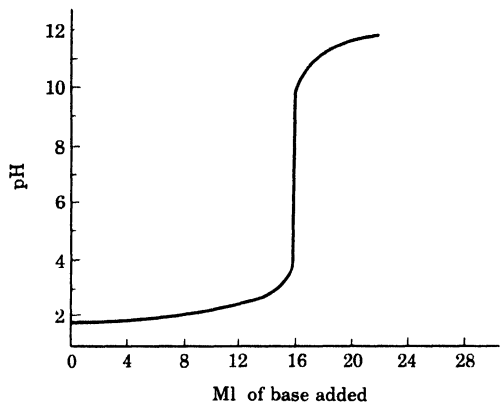


Fig. 11-3. pH titration of trimetaphosphoric acid. There is exactly one strongly acidic hydrogen per phosphorus according to the titration curve.

P_2O_5 in dehydrated $Na_3P_3O_9 \cdot II_2O$-I and as much as about 20% of the P_2O_5 in dehydrated $Na_3P_3O_9 \cdot H_2O$-II are found as a mixture of pyrophosphate and orthophosphate ions. Decomposition of these salts starts at around 100°C. and is at a maximum at about 200°C. At temperatures between 300 and 400°C., the decomposition products have recombined so that only anhydrous trimetaphosphate is found. This has been explained[40] on the basis of packing within the crystal, since the monohydrate exhibits a considerably smaller molecular volume for the component molecules and ions than does the sesquihydrate or the hexahydrate. If the molecular volume of water is computed by subtracting the mole volume of the anhydrous salt from the mole volume of the hydrated salt and then dividing the difference

[40] E. Moles and M. Crespi, *Z. phys. Chem.*, **130**, 137 (1927).

by the number of moles of water in the hydrate, the value for the monohydrates is about 5–9 ml./mole H_2O as compared to 11 and 15–18 in the sesqui- and hexahydrate, respectively. Approximately 14–16 ml./mole H_2O is usually found for simple hydrated salts;[40] and, in liquid water, there is 18 ml./mole H_2O. These calculations imply that, in the crystals of the two monohydrates, the water molecules are abnormally tightly wedged between the trimetaphosphate ring anions. The behavior of sodium trimetaphosphate monohydrate upon dehydration is similar to the degradation observed upon dehydrating the hexahydrate of sodium tripolyphosphate (see Chapt. 10, pp. 652–654), for which—by the way—the idea of abnormally close packing of the water molecules in the crystal does not hold. It should also be noted that $Li_3P_3O_9 \cdot 3\ H_2O$ undergoes extreme degradation upon heating.[41]

Sodium trimetaphosphate forms an addition compound with hydrogen peroxide,[17] $Na_3P_3O_9 \cdot H_2O_2$. Many preparations of this peroxidate are found to lose peroxide very easily since, in addition to the catalyzing effect of trace amounts of heavy metals on peroxide decomposition, the presence of other condensed phosphates in the sodium trimetaphosphate reduces the stability of the peroxide.[42] Several stabilizers have been suggested to improve the storability of $Na_3P_3O_9 \cdot H_2O_2$; and, of these, magnesium silicate and sodium aluminate appear to be the most satisfactory.

As previously mentioned, the acids corresponding to the ring phosphates are extremely strong. This is demonstrated by the *p*H titration curve of Figure 11-3, which shows the change in pH when either trimeta- or tetrametaphosphoric acid is titrated with tetramethylammonium hydroxide. According to the discussion of hydrolysis in Chapter 8 (pp. 452–459), the hydrolysis of trimeta- and tetrametaphosphate ions in dilute solution is catalyzed by both acid and base. A recent careful study of the hydrolysis of the trimetaphosphate ion in acidic and basic solutions has shown that there are several rate-processes going on at a given pH.[43] Some of this complicated behavior can be directly related to the formation of soluble complexes, such as $NaP_3O_9^{2-}$ and $CaP_3O_9^{-}$, and it is also conceivable that different configurations of the trimetaphosphate ion (as in a "boat" or "chair" form) can contribute to the complexity of the kinetics.

[41] H. Grunze and E. Thilo, *Z. anorg. u. allgem. Chem.*, **281**, 284 (1955); H. Grunze, *Angew. Chem.*, **67**, 408 (1955).

[42] Dr. Ness, *P. B. Report No.* **73716** (an English translation is available from Research Information Service, New York, as Report No. 5734).

[43] R. M. Healy and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **77**, 5258 (1955); also for the heat of hydrolysis (ΔH = 19.3 kcal./mole) see O. Meyerhof, R. Shatas, and A. Kaplan, *Biochim. et Biophys. Acta*, **12**, 121 (1953).

Ring Phosphates in Biology

In a recent paper, the existence of the trimetaphosphate ion in yeast extracts was described.[44] However, it is very probable[45] that the trimetaphosphate was formed as an artifact from the long chain phosphates normally found in year extracts. As pointed out in Chapter 12 (pp. 788–790), hydrolysis of long chain phosphates leads to the formation of small rings—especially the trimetaphosphate anion.

Preparation of Tetrametaphosphates

The classical method of preparing tetrametaphosphates is to heat monobasic orthophosphates of various heavy metals with a slight excess of phosphoric acid at about 300°C. or higher.[3–5,46] The resulting mass is then washed with water to leave a heavy metal tetrametaphosphate, soluble salts of which are prepared by appropriate metathesis reactions. Unfortunately, the early literature cannot be clearly interpreted as to which preparations are tetrametaphosphates in the modern sense of the word (a ring structure) and which are other materials exhibiting the metaphosphate composition. However, there is some recent literature to show that the tetrametaphosphates of cupric,[47,48] magnesium,[48] barium,[47] ferrous,[48] nickelous,[48] cobaltous,[48] manganous,[48] zinc,[48] cadmium,[48] plumbous,[30] and aluminum[7] ions can be made thermally. The zinc and cadmium metaphosphates can also be prepared (high temperatures) so as to have long chain instead of tetrameric rings as anions.[48] Soluble salts have been made from all of these tetraphosphates of multiply charged metal ions with the exception of the aluminum, magnesium, and nickel salts.

A standard preparation[47] is to mix copper nitrate with slightly more than an equimolar amount of phosphoric acid (75% H_3PO_4 is satisfactory) and then to heat this mixture slowly up to 400°C. in an unglazed porcelain dish. After cooling, the light-green product is ground in a mortar, washed in some water, and dried. Various tetrametaphosphates can be made from this copper salt, $Cu_2P_4O_{12}$, by treating it with either an ion exchange resin or a sulfide. The simplest preparation of sodium tetrametaphosphate is to add somewhat less than a stoichiometric amount of Na_2S—free from poly-

[44] S. R. Kornberg, *J. Biol. Chem.*, **218**, 23 (1956).

[45] J. P. Ebel in a private communication claims that the trimetaphosphate found by Mrs. Kornberg was wholly due to hydrolysis during the chemical procedures involved in isolation.

[46] F. Warschauer, *Z. anorg. Chem.*, **36**, 137 (1903).

[47] K. R. Andress, K. Fischer, and W. Gehring, *Z. anorg. Chem.*, **260**, 331 (1949).

[48] I. Born, *Angew. Chem.*, **67**, 409 (1955).

sulfides—to the copper salt, filter off the resulting precipitate of copper sulfide, and then to crystallize the $Na_4P_4O_{12}{\cdot}4\ H_2O$ after addition of NaCl or alcohol to reduce its solubility.

From 1849 to 1949, the literature dealing with tetrametaphosphates was concerned only with products made from thermally prepared heavy metal metaphosphates. However, it is now known that tetrametaphosphates can be made directly from the hexagonal crystalline form of phosphorus pentoxide[49–51] (P_4O_{10}), and this method of preparing tetrametaphosphates has been carried out on a commercial scale. By slowly adding P_4O_{10} to ice water, a yield in the neighborhood of 75% of the P_2O_5 in the form of tetrametaphosphoric acid can be achieved. In order to avoid hydrolysis, it is necessary to neutralize the acid to a pH of 7.0 very shortly after it is prepared. The decahydrate or tetrahydrate (depending on the temperature) of the sodium tetrametaphosphate can, by addition of NaCl, be readily crystallized out of the solution resulting from neutralization with NaOH or Na_2CO_3.

Although several authors have investigated the dissolution of P_4O_{10} in water, it was not until the work of Thilo and Wieker[51] that a satisfactory analytical procedure was employed in the study. These authors used paper chromatography in investigating the products of hydrolysis of P_4O_{10} and found in one experiment the results shown in Table 11-2. These results

TABLE 11-2
Hydrolysis of P_4O_{10} in Ice Water

	Percentage of total P			
Product of hydrolysis	Found by Thilo & Wieker	Calc. for equal rates	Calc. for reaction[a] 2 faster by 3.9×	Calc. for reactions[a] 2 & 6 faster by 3.9 & 3 5×
Tetrametaphosphate	77	20	77	77
Tetrapolyphosphate[b]	ca. 3	40	12	3
Trimetaphosphate	2	15	4	1
Tripolyphosphate	15	15	4	14
Orthophosphate	ca. 3	10	3	5

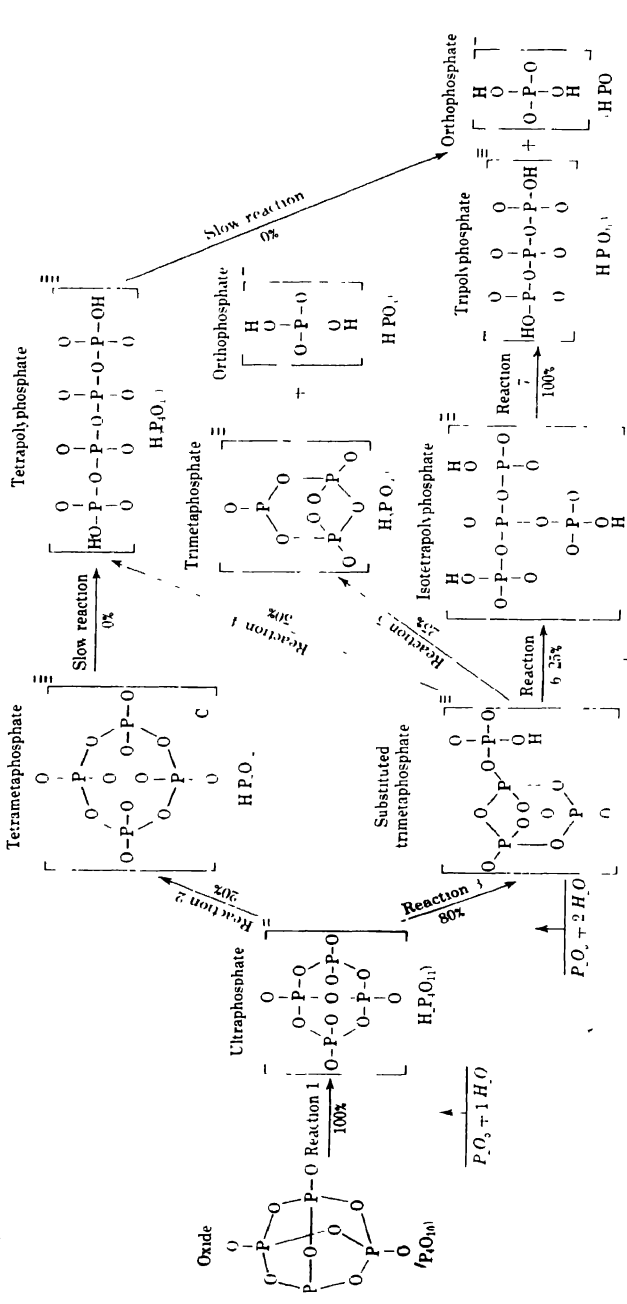
[a] The reactions refer to Figure 11-4.

[b] This value also includes higher phosphates.

[49] B. Raistrick, *Discussions Faraday Soc.*, **5**, 234 (1949).

[50] R. N. Bell, L. F. Audrieth, and O. F. Hill, *Ind. Eng. Chem.*, **44**, 570 (1952).

[51] E. Thilo and W. Wieker, *Z. anorg. u. allgem. Chem.*, **277**, 27 (1954).



g. 11-4 Hydrolysis of P_4O_{10}. Percentages under the arrows show the assumed relative amount of rapid breakdown via that path, as based on the false premise of equal probability for scission of all P—O—P linkages.

correspond to the experiment in which the largest amount of tetrametaphosphate was produced. Although Thilo and Wieker used a commercial grade of phosphorus pentoxide, it can safely be assumed that the greater part of this material consisted of P_4O_{10} molecules. A schematic representation of the hydrolysis of such P_4O_{10} molecules is given in Figure 11-4. In the only possible first step of the hydrolysis (labelled Reaction 1 in the figure), an ultraphosphate is produced. This ultraphosphate can break down by either of two paths (Reactions 2 or 3) to give tetrametaphosphate or a trimetaphosphate to which an end group is attached. Since the tetrametaphosphate is a known stable phosphate, the rapid part of the hydrolysis must end at this point. However, because of the branching point on the substituted trimetaphosphate, further rapid degradation should occur, as shown by Reactions 4, 5, and 6. Reaction 6 leads to an isotetrapolyphosphate, which also has a branching point, and should rapidly undergo further degradation by Reaction 7. If the scission of P—O—P linkages were completely independent of the position of the linkage, the reactions involved in the rapid hydrolysis of the P_4O_{10} would proceed according to the percentages shown under the arrows in Figure 11-4. In the second column of Table 11-2 the calculated distribution of the total phosphorus among the products of hydrolysis is shown based on this assumption of equal probability for scission of all of the P—O—P linkages in each structure.

Obviously, the calculation based on equal rates of P—O—P scission gives much too small a yield of tetrametaphosphate. However, if Reaction 2 is accelerated by a factor of 3.9, the yields given in the third column of Table 11-2 result. This means that the P—O—P linkage connecting the two branching points in the ultraphosphate structure is approximately four times more susceptible hydrolysis than the four other P—O—P linkages in the structure. Correction of the results by multiplying the probability of Reaction 2 by a factor of 3.9 still does not give proper results, since the calculated tetrapolyphosphate analysis is then too high, and the tripolyphosphate analysis is too low. Therefore, scission of the four P—O—P linkages in the substituted trimetaphosphate does not occur at equal rates. One might expect that the three P—O—P linkages connecting the branching point phosphorus with the other phosphorus atoms would be especially labile. However, the data indicate that the fourth P—O—P linkage connecting the two middle-group phosphorus atoms is the most susceptible to hydrolysis. If this linkage has an individual probability for scission 3.5 times greater than that of the other linkages, the experimental data can be accounted for, and the distribution of hydrolysis products based on this correction plus the correction to give higher weight to Reaction 2 agrees

quite well with the experimental findings as shown by comparison of the first and fourth columns of numbers in Table 11-2.

The third and simplest way of making tetrametaphosphates is to prepare the disodium dihydrogen salt.[23,52] By heating an equimolar mixture of monosodium orthophosphate and phosphoric acid at 400°C. and then slowly cooling the melt, the crystalline salt $Na_2H_2P_4O_{12}$ is formed. Crystallization of this material can be accelerated by stirring the melt for several minutes after the proper amount of water is driven off according to the following equation:

$$2\ NaH_2PO_4 + 2\ H_3PO_4 \xrightarrow{400°C} Na_2H_2P_4O_{12} + 4\ H_2O \qquad (11\text{-}4)$$

The tetrasodium salt can be made from the disodium salt by merely dissolving the latter in water and adding sufficient NaOH or Na_2CO_3 to bring the pH to 7.0. Sodium chloride can then be used to salt the tetrasodium tetraphosphate out of solution.

The preparation of a number of tetrametaphosphates of multiply charged or heavy metals by precipitation from solution has been described in the literature, mainly before 1900. Thus, Glatzel[5] lists about 20 hydrated salts which modern phosphate chemists would probably call tetrametaphosphates. Other authors[3,4,46] have also written about such salts. However, a listing of these salts—similar to Table 11-1—is not given here because (1) the discussions in most of the literature are obscured by false degrees of polymerization ascribed to the metaphosphate ion and (2) it is difficult to estimate the purity of the preparations. Since there appear to be both chain and ring forms of the thermally prepared metaphosphates of some of the heavy metals, it is quite probable that authors attempting to repeat each other's work without careful time-temperature control might in truth have been studying radically different substances or mixtures.

Proof of the Tetrametaphosphate Structure

The first structure analysis[7] leading to interatomic distances in a condensed phosphate other than the pyrophosphate was carried out on aluminum tetrametaphosphate. This study showed that the tetrameta anion is a ring made up of four interconnected PO_4 groups—*i.e.*, an eight-membered ring of alternate phosphorus and oxygen atoms. However, aluminum tetrametaphosphate cannot be put into solution without decomposi-

[52] E. J. Griffith, *J. Am. Chem. Soc.*, **76**, 5892 (1954).

tion of the anion, and hence the determination of its structure is not of outstanding chemical interest.

The evidence that soluble tetrametaphosphates, such as $Na_4P_4O_{12}$, exhibit an anion made up of a ring of four phosphorus atoms alternating with oxygen atoms is similar to the evidence that soluble trimetaphosphates have a similar cyclic anion containing three phosphorus atoms. However, the x-ray work on the tetrametaphosphate ion is probably conclusive proof of the structure in itself. The major proofs for the structure of the tetrametaphosphate anion are briefly noted in the following tabulation.

1. X-ray structure studies show that the tetrametaphosphate ion consists of a ring made up of four PO_4 tetrahedra linked together by the sharing of two corner oxygen atoms apiece. This conclusion is based primarily on symmetry considerations in the case of $Al_4(P_4O_{12})_3$ (insoluble)[7] and $Na_4P_4O_{12}\cdot 4\ H_2O$;[47] but it rests on a very detailed structure analysis in the case of $(NH_4)_4P_4O_{12}$.[53,54]

2. The nuclear magnetic spectrum[31] of phosphorus in solutions of the tetrametaphosphate ion as well as the titration curve[32,33] of tetrametaphosphoric acid show that all phosphorus atoms are in middle groups.

3. Careful measurements[33] of the conductance of dilute solutions of sodium tetrametaphosphate and tetrametaphosphoric acid show that these compounds dissociate into a singly charged cation and a quadruply charged anion, when a small correction is made for some ion association to $[NaP_4O_{12}]^{3-}$.

4. Cryoscopic determinations[55] in sodium sulfate decahydrate gave molecular weights of 414 and 417 as compared to the theoretical value of 408 for $Na_4P_4O_{12}$. In water as a solvent, the molecular weight was found to agree with the supposition of a quadruply charged anion better than with any other assumption.[34]

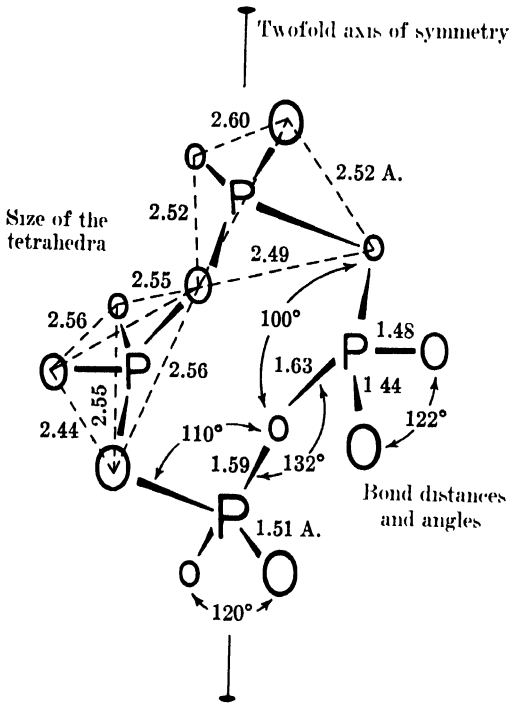
5. The presence of four phosphorus atoms per ring is suggested by the high yield of sodium tetrametaphosphate in the hydrolysis of phosphorus pentoxide.[49,51] The formation of a preponderance of tetrapolyphosphate in the alkaline hydrolysis of tetrametaphosphate is also some indication that the ring structure with four phosphorus atoms for the latter is correct.[36]

The x-ray study by Romers, Ketelaar, and MacGillavry[54] of the structure of ammonium tetrametaphosphate made from the copper salt has led to the interatomic distances and angles for the anion shown on the next page.

[53] J. A. A. Ketelaar and C. H. MacGillavry, *Nature*, **164**, 960 (1949); K. R. Andress and K. Fischer, *Acta Cryst.*, **3**, 399 (1950).

[54] C. Romers, J. A. A. Ketelaar, and C. H. MacGillavry, *Acta Cryst.*, **4**, 114 (1951).

[55] P. Bonneman, *Compt. rend.*, **204**, 865 (1937).



(11-5)

(Distances in A and angles in degrees)

As can be seen from the PO_4 groups in which the distances between oxygen atoms are shown, the PO_4 tetrahedra are nearly regular, the edges being 2.51 ± 0.05 A., which may well be a constant within the experimental error. The phosphorus atoms, however, are not centrally located within the tetrahedra but are shifted away from the oxygen atoms common to two tetrahedra. This corresponds to an excess of π-character in the bonds to the unshared oxygens. It should be noted that the ammonium ions have four oxygen atoms as nearest neighbors in the crystal structure, and that the unshared oxygens are closer (2.82 A.) to the nitrogen atoms of the ammonium ions than are the bridging oxygens (3.3 A.). This has been interpreted as evidence that there are hydrogen bonds between the unshared oxygens of the PO_4 groups and the nitrogens of the ammonium ions; however, it might also be attributed to a localization on the unshared oxygen atoms of the negative charges due to ionization of the phosphate anion.

Boat and Chair Forms

Recent studies by Gryder[56] and associates[57] have indicated that there may be two different configurations of the tetrametaphosphate anion which are stable enough in solution so that they can be isolated as different salts. Spacial diagrams of these two configurations, called the "boat" and "chair" forms, are shown in Figure 11-5. The chair form is the one on which a

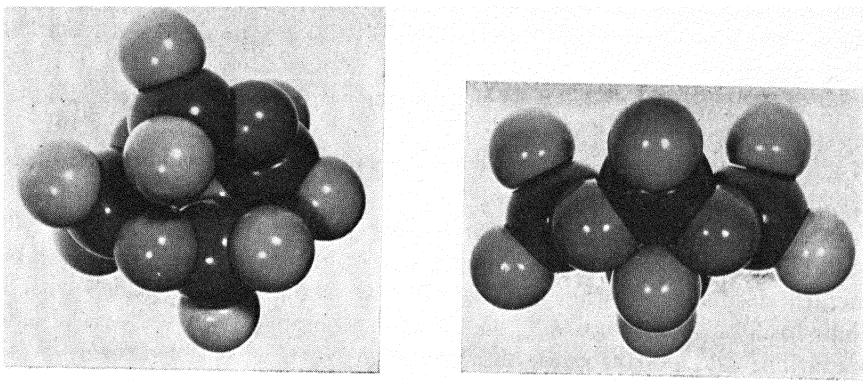


Fig. 11-5. Spacial diagrams showing the boat (left) and chair (right) forms of the tetrametaphosphate anion, according to Gryder.

structure determination was made by Romers, Ketelaar, and MacGillavry.[54] It is the variety prepared from the copper salt. On the other hand, the boat form is made by low-temperature hydrolysis of P_4O_{10}. In aqueous solution, the boat form slowly converts to the chair form, and the equilibrium between the two must be rather far on the side of the chair form, since the reverse of this process does not seem to happen to any extent. At room temperature and neutral pH, conversion of the boat to the chair form takes many hours.

Proof[56] that the two forms correspond to different configurations of the anion and are not simply polymorphic varieties of crystals is based on the following circumstantial evidence:

1. There are two varieties of $Na_4P_4O_{12} \cdot 4\ H_2O$, two varieties of $K_4P_4O_{12} \cdot 4\ H_2O$, two varieties of anhydrous $(NH_4)_4P_4O_{12}$, and two varieties of anhydrous $K_4P_4O_{12}$. In every case, the boat variety of the potassium or ammonium salts must be made from the boat variety of the sodium salt, and the

[56] J. W. Gryder, private communications from Johns Hopkins University.

[57] R. J. Gross, J. W. Gryder, and G. Donnay, *Abstracts of Papers from 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, Sept. 11–16, 1955.*

chair variety must be made from the chair sodium salt (which, of course, may be obtained by reversion of the boat variety in solution). Anhydrous $Na_4O_4O_{12}$ is only known as the chair form, and $(NH_4)_4P_4O_{12} \cdot 5\ H_2O$ is only known as the boat form.

2. Precipitation with alcohol under identical conditions at various temperatures gives either the chair or the boat form, depending on which was present in the starting solution. Thus, only a boat crystal can be obtained from a boat solution (unless time is allowed for conversion of the boat to the chair form in solution), and only a chair crystal can be obtained from the chair solution.

3. Mixtures of the boat and chair forms can be separated by fractional crystallization.

4. Seeding with the opposite form does not cause this opposite form to crystallize from solution.

5. If the operation is carried out quickly and carefully, the silver salt obtained from a given tetrametaphosphate solution by precipitation can be metathesized back to the original salt with NaCl. If one starts with a chair form of the sodium salt, one obtains a chair form at the end of this operation; and a boat form is obtained if one starts with a boat form.

6. The boat and chair forms are said[56] to give separable spots on a two-dimensional paper chromatogram.

It should be noted that work by previous investigators[41,50] showed up the existence of some of these pairs of forms ascribed by Gryder to boat and chair modifications. However, the other investigators felt that they had ample evidence to consider the different varieties as simply polymorphic crystalline forms, since they did not observe the phenomena listed under items 2 and 4 above, and they did not investigate item 3. This problem—as to whether different configurations of the tetrametaphosphate anion persist in solution and can be resolved—is an interesting one on which, at the time of this writing (early 1957), considerable further work is needed.

Properties of the Tetrametaphosphates

The disodium dihydrogen tetrametaphosphate exhibits a unique x-ray pattern and melts at 400°C. This compound is readily soluble in water, and its 1% solutions have a pH of 1.2. Tetrasodium tetrametaphosphate is known in the form of the decahydrate, two tetrahydrates, and the anhydrous salt. Solubilities[39] of the decahydrate and the two tetrahydrates are shown in Figure 11-6. An irreversible transition of the variety designated as the boat form of the tetrahydrate to that designated as the chair

form upon heating to the temperature of 54°C. has been reported in the literature,[50] but the existence of this transition has been disputed by Gryder.[56] It is reported[41,50] that the deca- and tetrahydrates of sodium tetrametaphosphate are easily dehydrated thermally to anhydrous sodium tetrametaphosphate without decomposition of the phosphate structure. However, $Li_4P_4O_{12} \cdot 4\ H_2O$ and $K_4P_4O_{12} \cdot 2\ H_2O$ undergo partial hydrolytic decomposition upon being heated in air.[41] At temperatures around 400°C., anhydrous sodium tetrametaphosphate is irreversibly transformed to sodium

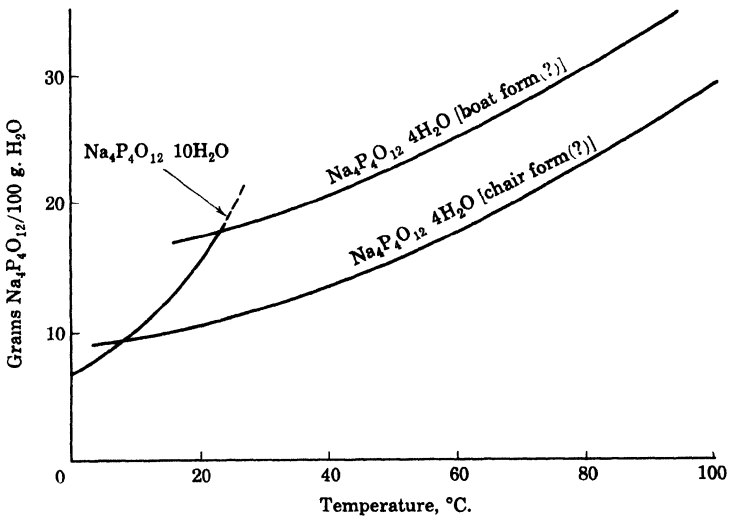


Fig. 11-6. Solubility of sodium tetrametaphosphate showing the two forms of the tetrahydrate.

trimetaphosphate[50,58] and cannot be regained by any known subsequent treatment of the sodium trimetaphosphate other than by employing the methods described above for tetrametaphosphate synthesis.

In alkaline solution, the tetrametaphosphate anion hydrolyzes more than ten times slower than does the trimetaphosphate anion, and the activation energy for the hydrolytic degradation is about 30% larger in the case of tetrametaphosphate anion.[59] These differences are probably explainable on the basis that the tetrametaphosphate ring exhibits a greater number of possible atomic configurations and modes of internal motion than does the

[58] A. Boullé, *Compt. rend.*, **206**, 1732 (1938).
[59] I. A. Brovkina, *Zhur. Obshcheĭ Khim.*, **22**, 1917 (1952).

trimetaphosphate ion, so that the latter is essentially more rigid and hence more subject to scission. It is interesting to note that although sodium trimetaphosphate forms a peroxidate, no such double salt between sodium tetrametaphosphate and hydrogen peroxide is known.[17]

Ring Compounds Larger than the Tetrametaphosphate

When this chapter was first laid out in rough draft early in 1956, there were no reports of the existence of ring phosphates larger than the tetrameta. However, a search for such substances in Graham's salt (vitreous $NaPO_3$) led to success.[60] As shown in Figure 11-7, individual spots for

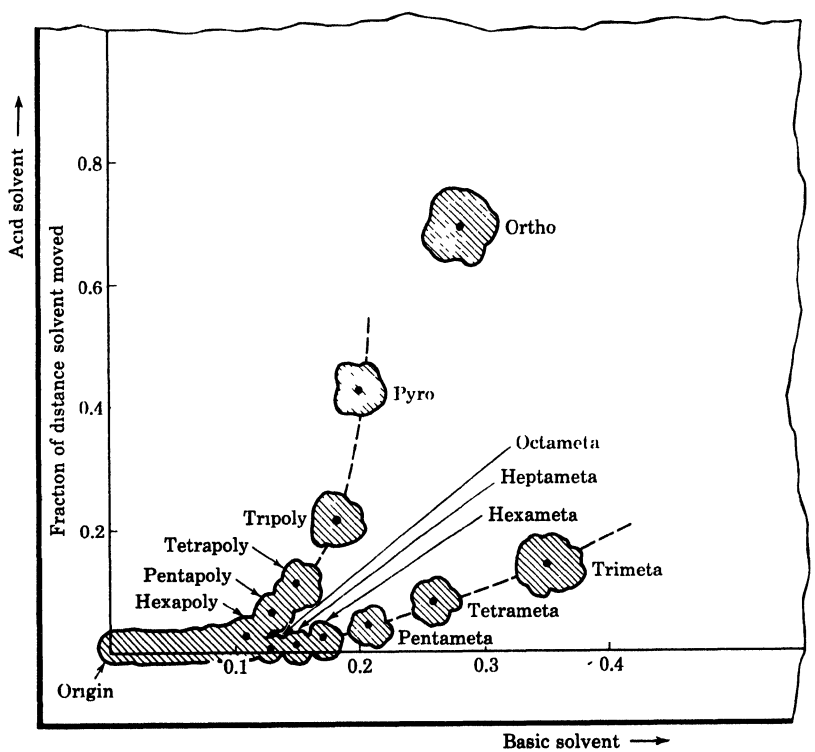


Fig. 11-7. Corner of a two-dimensional paper chromatogram showing the positions of the pentameta- through octametaphosphate rings in relation to the positions of the well-known ring and chain phosphates. The basic solvent went 9 in. in 24 hr., whereas the acid solvent went 4.5 in. in 5.5 hr.

[60] J. R. Van Wazer and E. Karl-Kroupa, *J. Am. Chem. Soc.*, **78**, 1772 (1956).

rings containing as many as six to eight phosphorus atoms have been observed. Furthermore, the chromatograms show that the continuum of overlapping spots due to the higher ring phosphates forms a Y with the continuum of overlapping spots due to the unresolved chain phosphates. Indeed, the appearance of selected chromatograms in which especially good

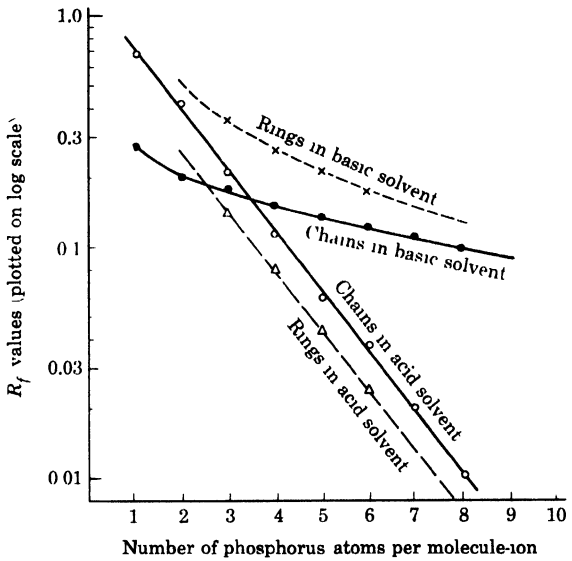


Fig. 11-8 Some typical R_f values in paper chromatography of phosphates using Ebel's technique.[61] (R_f equals ratio of the distance the solvent front moved to the distance moved by the spot.)

resolution was achieved on Graham's salt using the basic solvent indicates the existence of large rings containing about 20 atoms (10 phosphorus and 10 oxygen atoms) per ring.

The technique of two-dimensional paper chromatography whereby rings are clearly and distinctly separated from chains was developed by Ebel.[61] A typical chromatogram is shown in Figure 11-7, and the R_f values corresponding to this pair of solvents are given in Figure 11-8. It should be noted in these figures that the determination of rings much higher than the

[61] J. P. Ebel, *Bull. soc. chim. France*, **20**, 991, 998 (1953); also see E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

octametaphosphate becomes difficult by paper chromatography, and that high molecular weight rings cannot be distinguished from high molecular weight chains. The chromatographic procedure would be suitable for showing up the presence of dimetaphosphate rings; but, in this case, extremely rapid hydrolysis in aqueous solvents would be expected, so that the chromatograms would probably only show pyrophosphate if dimetaphosphate rings were really present in the anhydrous sample.

Other possible methods for finding large ring phosphates are solubility fractionation by barium precipitation or salting out with organic liquids.[62] The trimetaphosphate ion is not readily precipitated by barium, and the tetrametaphosphate ion gives a somewhat more insoluble precipitate but is still sufficiently soluble to give no precipitation at the low concentrations usually used in analytical techniques. Presumably, chain phosphates can be removed from the ring phosphates by precipitation by barium or other heavy metal ions in dilute solution, and ring phosphates could be fractionated from each other by addition of the heavy metal ion at relatively high concentrations. Combination of barium precipitation (to remove chain phosphates) with chromatography (using high spot concentrations to accentuate the presence of small amounts of rings) may offer a fruitful approach for the detection of unknown phosphate ring species.

Soluble Complexes of the Ring Phosphates

Although the complexing ability of the ring phosphates is weak as compared to that of the chain analogs (so weak, in fact, as to be of no commercial value), there have been more precise measurements of the complexing by ring than by chain phosphates[63] -probably because the investigators felt more sure of the identity and molecular weight of the ring compounds. The dissociation constants found for various soluble complexes of the trimeta- and tetrametaphosphate anions are presented in Tables 11-3 and 11-4, respectively. It should be noted that in computing a number of the dissociation constants reported in these tables for ions other than sodium, no correction was made for the metaphosphato-sodium complex.

[62] J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 647 (1950).

[63] C. W. Davies and C. B. Monk, *J. Chem. Soc.*, **1949**, 413; H. W. Jones, C. B. Monk, and C. W. Davies, *ibid.*, **1949**, 2693; H. W. Jones and C. B. Monk, *ibid.*, **1950**, 3475; C. B. Monk, *ibid.*, **1952**, 1314, 1317; R. J. Gross and J. W. Gryder, *J. Am. Chem. Soc.*, **77**, 3695 (1955); R. E. Gosselin and E. R. Coghlan, *Archiv. Biochem. and Biophys.*, **45**, 301 (1950); D. Campanella, G. Deckey, and J. R. Van Wazer, unpublished data obtained at the Rumford Chemical Works.

TABLE 11-3

Trimetaphosphate Complexes of Various Metals[63]

Metal complexed	Total conc. metal ion (moles/l.)	Moles P/ moles M	Other conditions[a]	Average pK$_D$ reported by investigator[b]	Method
H	$3\,0 \times 10^{-4}$	1 0	$t = 25$	2 05 ± 10%[c]	Electrical
	$11\,6 \times 10^{-4}$	1 0	$t = 25$	2 05 ± 10%[c]	conductivity
Na	$1\,2 \times 10^{-4}$	1 0	$t = 25$	1 17[c]	Electrical
	$8\,8 \times 10^{-4}$	1 0	$t = 25$	1 17[c]	conductivity
Ca	$3\,60 \times 10^{-4}$	2 8	$t = 25$	3 45[d,c]	Electrical
	$14\,3 \times 10^{-4}$	0 68	$t = 25$	3 45[d,c]	conductivity
Ca	$1\,40 \times 10^{-4}$	>100	$t \backsimeq 25$ pH = 8	2 6[e]	Solubility $CaHPO_4$
Ca	$9\,06 \times 10^{-3}$	1 1	$t = 25$	3 48[e,f]	Solubility
	$13\,17 \times 10^{-3}$	4 6	$t = 25$	3 48[e,f]	$Ca(IO_3)_2$
Ca	ca. 9×10^{-4}	$>10^3$	$\mu \backsimeq 0\,15$ pH = 7 4 $t = 37$	2 50[g]	Ion exchange equilibria
Sr	$1\,92 \times 10^{-4}$	4 41	$t = 25$	3 35[d,c]	Electrical
	$6\,3 \times 10^{-4}$	1 80	$t = 25$	3 35[d,c]	conductivity
Sr	$7\,54 \times 10^{-3}$	2 17	$t = 25$	3 35[e,f]	Solubility
	$8\,67 \times 10^{-3}$	3 67	$t = 25$	3 35[e,f]	$Sr(IO_3)_2$
Ba	$1\,76 \times 10^{-4}$	6 0	$t = 25$	3 35[d,c]	Electrical
	$8\,1 \times 10^{-4}$	1 28	$t = 25$	3 35[d,c]	conductivity
Mg	$2\,92 \times 10^{-4}$	2 52	$t = 25$	3 31[d,c]	Electrical
	$13\,0 \times 10^{-4}$	0 55	$t = 25$	3 31[d,c]	conductivity
Mn	$3\,76 \times 10^{-4}$	2 52	$t = 25$	3 56[d,c]	Electrical
	$12\,3 \times 10^{-4}$	0 75	$t = 25$	3 56[d,c]	conductivity
Ni	$1\,52 \times 10^{-4}$	4 14	$t = 25$	3 21[d,c]	Electrical
	$6\,55 \times 10^{-4}$	0 94	$t = 25$	3 22[d,c]	conductivity
La	$2\,10 \times 10^{-4}$	4 58	$t = 25$	5 70[c,h]	Electrical
	$5\,81 \times 10^{-4}$	3 03	$t = 25$	5 70[c,h]	conductivity
$Co(NH_3)_6^{3+}$	$1\,37 \times 10^{-4}$	7 32	$t = 25$	4 44[c,h]	Electrical
	$4\,92 \times 10^{-4}$	2 33	$t = 25$	4 44[c,h]	conductivity
$Co(en)_3^{3+}$	$0\,41 \times 10^{-4}$	8 12	$t = 25$	4 40[c,h]	Electrical
	$4\,92 \times 10^{-4}$	2 34	$t = 25$	4 40[c,h]	conductivity
$Co(pn)_3^{3+}$	$1\,84 \times 10^{-4}$	6 37	$t = 25$	3 65	Electrical
	$5\,64 \times 10^{-4}$	1 88	$t = 25$	3 65	conductivity

[a] μ is the ionic strength, t the temperature in °C.

[b] Negative logarithm equilibrium dissociation constants for the 1:1 metal-to-phosphate molecule complex in which all ionizable hydrogens are removed from the phosphate molecule (unless otherwise designated).

[c] Debye-Huckel limiting theoretical activity coefficients applied.

[d] Correction made for assumed presence of $NaP_3O_9^{2-}$.

[e] Solubility product of $CaHPO_4$ at pH of 8 assumed to be 5×10^{-5}.

[f] Allowance made for the species MIO_3^+, $NaIO_3$, and $NaP_3O_9^{2-}$.

[g] Activity coefficients assumed to be unity, and total phosphate concentration was used as the concentration of the complexing anion (free of ionizable hydrogens).

[h] Allowance made for the species $NaP_3O_9^{2-}$, MCl^{2+}.

TABLE 11-4
Tetrametaphosphate Complexes of Various Metals

Metal complexed	Total conc. metal ion (moles/l.) (range)	Moles P/ moles M	Other conditions[a]	Average pK$_D$ reported by investigator[b]	Method
H	3.46×10^{-4}	1.0	$t = 25$	2.74[c]	Electrical
	11.6×10^{-4}	1.0	$t = 25$	2.74[c]	conductivity
Na	4.19×10^{-4}	1.0	$t = 25$	2.05[c]	Electrical
	14.4×10^{-4}	1.0	$t = 25$	2.05[c]	conductivity
Ca	2.17×10^{-4}	4.25	$t = 25$	5.42[c,d]	Electrical
	5.52×10^{-4}	1.58	$t = 25$	5.42[c,d]	conductivity
Ca	9.96×10^{-5}	1.34	$t = 25$	4.89[c,g]	Solubility
	12.6×10^{-3}	2.29	$t = 25$	4.89[c,e]	$Ca(IO_3)_2$
	9.96×10^{-3}	1.34 to	$t = 25$	2.66[c,f]	Solubility
	to 12.6×10^{-3}	2.29			$Ca(IO_3)_2$
Ca	11.2×10^{-5}	1.86	$t = 25$	5.32[c,g]	Solubility
	17.7×10^{-3}	3.33	$t = 25$	5.32[c,g]	$Ca(IO_3)_2$
Ca	ca. 9×10^{-6}	$>10^3$	$\mu \approx 0.15$		
			pH = 7.4	3.36	Ion exchange
			$t = 37$		equilibria
Sr	0.80×10^{-4}	8.58	$t = 25$	5.15[c,d]	Electrical
	5.53×10^{-4}	2.45	$t = 25$	5.15[c,d]	conductivity
Sr	9.33×10^{-3}	2.45	$t = 25$	5.08[c,h]	Solubility
	12.9×10^{-3}	3.67	$t = 25$	5.08[c,h]	$Sr(IO_3)_2$

[a] μ is the ionic strength, t the temperature in °C.

[b] Negative logarithm equilibrium dissociation constants for the 1:1 metal-to-phosphate molecule complex in which all ionizable hydrogens are removed from the phosphate molecule (unless otherwise designated)

[c] Debye-Huckel limiting theoretical activity coefficients applied.

[d] Allowance made for species $NaP_4O_{12}^{3-}$, $M_2P_4O_{12}$, and $NaMP_4O_{12}^{-}$.

[e] Allowance made for species MIO_3^{+}, $NaIO_3$, $NaP_4O_{12}^{3-}$, $M_2P_4O_{12}$.

[f] Negative logarithm dissociation constant for the equilibrium $Ca_2P_4O_{12} \rightleftharpoons Ca^{2+} + CaP_4O_{12}^{2-}$.

[g] Allowance made for species MIO_3^{+}, $NaIO_3$, $NaP_4O_{12}^{3-}$, $M_2P_4O_{12}$, and $NaMP_4O_{12}^{-}$.

[h] Negative logarithm dissociation constant for the equilibrium $M(P_4O_{12})_2^{6-} \rightleftharpoons M^{2+} + 2\ P_4O_{12}^{-4}$.

BRANCHED PHOSPHATES

General Considerations

In Chapter 8 (pp. 437–441), a discussion is given of the statement: "In any environment in which reactions involving the degradation of con-

TABLE 11-4 (*continued*)

Metal complexed	Total conc. metal ion (moles/l.) (range)	Moles P/ moles M	Other conditions[a]	Average pK_D reported by investigator[b]	Method
Ba	$1\ 25 \times 10^{-4}$	6 34	$t = 25$	4 99[c,d]	Electrical
	$3\ 84 \times 10^{-4}$	2 02	$t = 25$	4 99[c,d]	conductivity
Mg	$0\ 84 \times 10^{-4}$	9 24	$t = 25$	5 17[c,d]	Electrical
	$2\ 76 \times 10^{-4}$	2 72	$t = 25$	5 17[c,d]	conductivity
Mn	$1\ 61 \times 10^{-4}$	5 20	$t = 25$	5 74[c,d]	Electrical
	$8\ 86 \times 10^{-4}$	1 62	$t = 25$	5 74[c,d]	conductivity
Ni	$0\ 79 \times 10^{-4}$	10 1	$t = 25$	4 95[c,d]	Electrical
	$5\ 83 \times 10^{-4}$	2 31	$t = 25$	4 95[c,d]	conductivity
Ni	$2\ 58 \times 10^{-3}$	4 85	$t = 30$	2 63	Potentiometric
	$2\ 58 \times 10^{-3}$	19 5	$\mu = 1\ 0$	2 63	in presence of
	$10\ 28 \times 10^{-3}$	1 44		2 63	Cu^{2+}
	$10\ 28 \times 10^{-3}$	5 01		2 63	
Ni	2 58 to	1 4 to	$t = 30$	3 48[h]	Potentiometric
	$10\ 28 \times 10^{-3}$	19 5	$\mu = 1\ 0$		
Cu	$2\ 58 \times 10^{-3}$	3 46	$t = 30$	3 18	Potentiometric
	$2\ 58 \times 10^{-3}$	6 92	$\mu = 1\ 0$	3 18	
	$2\ 58 \times 10^{-3}$	27 6		3 18	
Cu	$2\ 58 \times 10^{-3}$	3 5 to	$t = 30$	4 64	Potentiometric
		27 6	$\mu = 1\ 0$		

densed phosphates are possible, it is to be expected that assemblies in which three of the four oxygens of a PO_4 tetrahedron are shared with other PO_4 tetrahedra will be exceedingly unstable and will degrade much more rapidly as compared to those in which one or two oxygens are shared." According to this statement—usually called the Antibranching Rule—branching points should not be found in equilibrium phosphate compositions unless the M_2O/P_2O_5 ratio is less than unity. This means that equilibrium structures involving branching points are to be found only in the ultraphosphate range of composition (pure P_2O_5 to $M_2O{\cdot}P_2O_5$). However, it is conceivable that substances having a M_2O/P_2O_5 ratio considerably greater than unity might be prepared so as to contain some branching points if they were made by fractionating ultraphosphate compositions or if intermediate structures were frozen into a final composition. An example of such substances is found in the condensation products of ammonia and phosphorus pentoxide, as made by combining a stream of phosphorus pentoxide vapor with ammonia and quenching. In the normally produced

mixtures of these substances, there are occasional crosslinkages left over from incomplete breaking of the branching points originally present in the P_4O_{10} molecule. (These compounds are discussed on pp. 841–843.)

Preparation of Ultraphosphates

The usual procedure for making ultraphosphates is to mix phosphorus pentoxide with an appropriate salt of the metaphosphate composition and then to heat the resultant mixture to effect reaction. Since the ultraphosphates readily react with the water vapor normally present in air, even at elevated temperatures, it is usually necessary to heat ultraphosphates in completely dry atmospheres. This can be done either in a platinum dish enclosed in a tightly sealed furnace or by sealing the reaction mixture into a glass or silica tube. In the latter case, precautions must be taken to avoid undue contamination with silica, and preparations made in a sealed tube should always be analyzed for SiO_2.

The avidity with which sodium ultraphosphates take up water is demonstrated by the preparation of sodium acid metaphosphates.[23] While trying to make sodium ultraphosphates from a mixture of sodium metaphosphate and phosphorus pentoxide in a platinum dish at 300–400°C. in a regular muffle furnace, it was found that enough water was taken up to bring the over-all composition to that of the metaphosphate. In this work it was also discovered that the addition of a small amount of sodium nitrate apparently catalyzes the formation of higher molecular weight ultraphosphates in the melt, since fuming of the ultraphosphate melts was greatly reduced by the addition of about one per cent of sodium nitrate.

In the case of the phosphoric acids, ultraphosphates can be made by thermal dehydration of compositions having excess water. As shown by Figure 12-22, ultraphosphoric acids exhibiting as much as 32.5% of the total P_2O_5 as branching points can be formed by merely heating orthophosphoric acid. Azeotropic phosphoric acid,[64] which is the most branched acid obtainable by dehydration, has an H_2O/P_2O_5 mole ratio of 0.675–0.770 and boils in the range of 870–695°C., depending on the pressure

Structure and Properties of the Ultraphosphates

Since very little effort has been put on studying the ultraphosphate range of composition, only two crystalline ultraphosphates are known with certainty. These are the compounds $CaO{\cdot}2\ P_2O_5$ and $2\ CaO{\cdot}3\ P_2O_5$, which are

[64] G. Tarbutton and M. E. Demming, *J. Am. Chem. Soc.*, **72**, 2086 (1950).

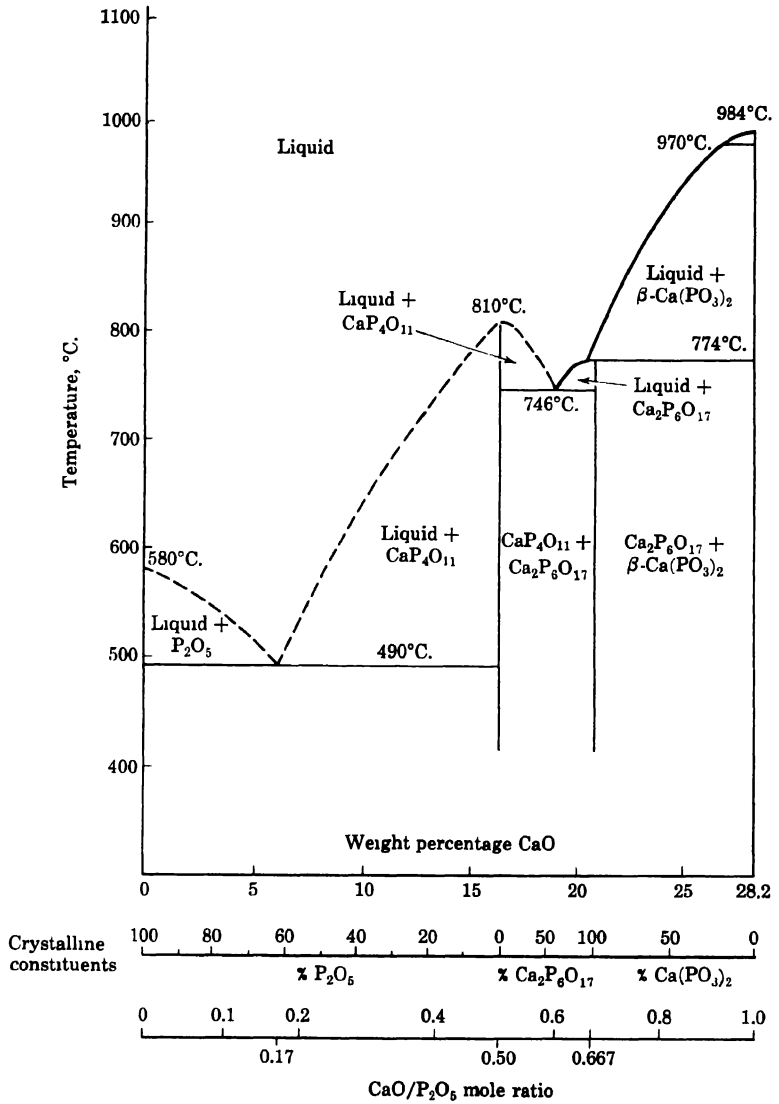


Fig. 11-9. The portion of the $CaO–P_2O_5$ phase diagram between $CaO \cdot P_2O_5$ and pure P_2O_5.

found in the phase diagram of Hill, Faust, and Reynolds.[65] The ultraphosphate part of this diagram is shown in Figure 11-9. Both of these

[65] W. L. Hill, G. T. Faust, and D. S. Reynolds, *Am. J. Sci.*, **242**, 457, 542 (1944).

crystalline calcium ultraphosphates are extremely slowly soluble in water Tests of these materials as fertilizers have indicated that both of them are slowly available to plants, and that they hydrolyze about as quickly as they dissolve. No molecular structure studies have as yet been carried out on these materials; but, presumably, they exhibit relatively simple structures, such as are shown in Table 11-5.

Most of the work on ultraphosphates has been concerned with vitreous compositions. Thus, Kroll[8] describes ultraphosphates of lithium, sodium, potassium, calcium, silver, platinum, and lead. Five years later, a vitreous sodium ultraphosphate was again described,[65] and, in the recent literature, more systematic studies were made of lithium, sodium,[66,62] and cadmium glasses in the ultraphosphate region of composition. A detailed discussion of these vitreous ultraphosphates is presented in Chapter 12, pages 790–791. The compounds near the metaphosphate composition which exhibit a small amount of branching (and, hence, are limiting ultraphosphates) are described in Chapter 10, page 676.

One of the interesting properties of the vitreous ultraphosphates that have been studied thus far is slow solubility, which has been attributed to the crosslinking occurring in their structures.[62] Some of these ultraphosphates decrepitate violently in water.[8] An example of this is crackling "metaphosphoric acid" (really an ultraphosphate). Such substances when brought in contact with water produce a crackling, singing noise which is caused by small particles breaking away from the surface with considerable violence. If the layer of water over the solid ultraphosphate is not too thick (only a few millimeters), the tiny particles shooting out of the surface of the ultraphosphate can actually bombard the hand with enough force to cause a mild sensation of pain. Presumably, the crackling effect is due to the hydrolysis of crosslinks lying at the boundaries of regions of the solid not yet attacked by the water. The formation of OH groups by hydrolysis at branching points (crosslinks) causes a potential volume increase which builds up sufficient stress to rupture the solid.

Hypothetical Structures for the Simple Ultraphosphates

It was shown in Chapter 8, pages 435–436, that the ultraphosphates of lowest molecular weight will exhibit formulas in which the M_2O/P_2O_5 mole ratio, R, is a proper fraction having small whole numbers in the numerator and denominator. In the general formula,

$$M_{nR}P_nO_{n(5+R)/2} \qquad (11\text{-}6)$$

[66] J. H. Smith, *J. Soc. Chem. Ind.*, **36**, 419 (1917); E. Kordes and H. Becker, *Z. anorg. Chem.*, **260**, 185 (1949); also see A. Sonntag, *Angew. Chem.*, **67**, 409 (1955).

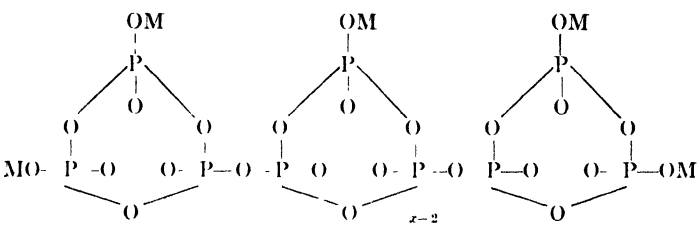
it was shown that, when the sum of the numerator plus the denominator of R is even, $n_{min.}$ equals the denominator of R. And, when the numerator plus denominator is odd, $n_{min.}$ equals twice the denominator—where $n_{min.}$ is the number of phosphorus atoms in the smallest possible structure corresponding to a given value of R.

In Table 11-5, some possible structures for various small proper-fraction values of the M_2O/P_2O_5 ratio are presented. Except for the simplest structures corresponding to $R = {}^1/_3$ and $R = {}^1/_5$, the examples given in Table 11-5 do not show strain when assembled from spacial atomic models. In the two cases where $R = {}^1/_3$ and $R = {}^1/_5$, the dimer of the simplest structure is strain free. In Table 11-5, it should be noted that there are a number of different spacial configurations possible for nearly all of the structures, and that the three-dimensional structures shown represent just one of these configurations for each formula.

Some Ultraphosphate Families

Since the general formula for all phosphates (equation 11-6) reduces to simple formulas in which R is not a parameter in the case of the meta- and polyphosphate compositions, it is instructive to derive similar simple formulas (in which R is not a parameter) for the ultraphosphate region. One way to do this is to assume an ultraphosphate family in which structural units are repeated in a regular fashion, and this has been done in the following paragraphs for two examples: (1) rings directly attached to each other so as to form long chains of interconnected rings and (2) rings alternating with chains so as to form complicated chain-like structures.

First let us consider a hypothetical structural system composed of coupled trimeta rings, as shown below:



(11-7)

By adding more and more rings, the sequences of chemical formulas given in Table 11–6 are obtained. It should be noted that, according to the rules given above, all of these formulas give the smallest possible structures corresponding to their R values—except for the compound, $M_6P_{12}O_{33}$, which is three times larger than the smallest structure (see Table 11-5).

TABLE 11-5 Some Possible Structures for Some Small Ultraphosphates

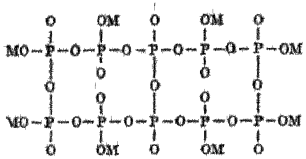
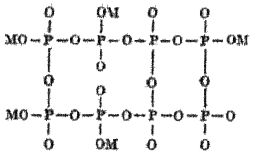
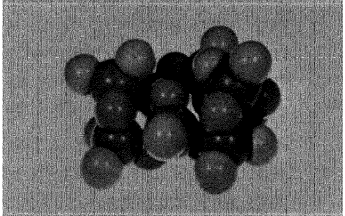
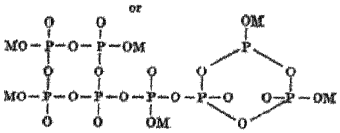
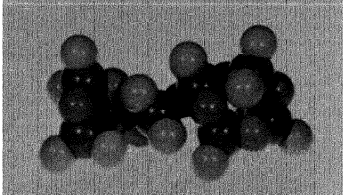
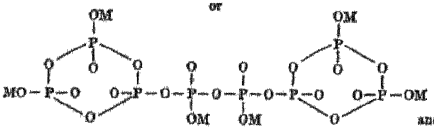
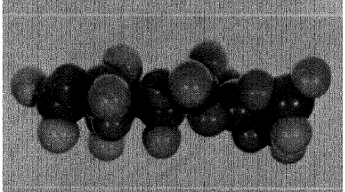
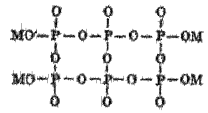
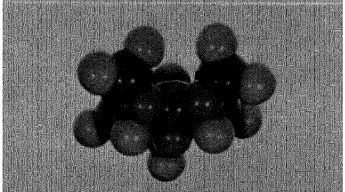
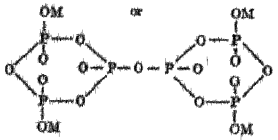
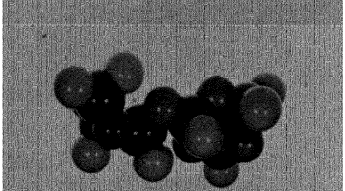
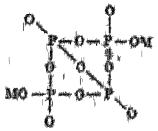
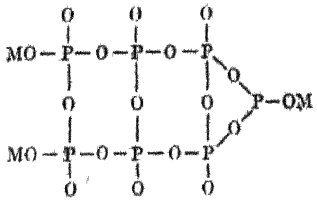
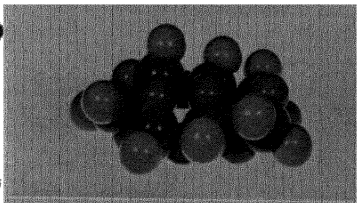
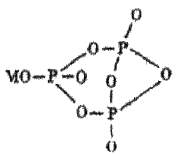
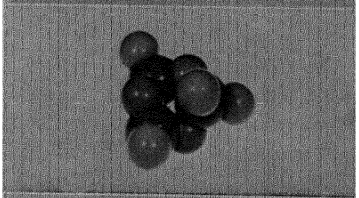
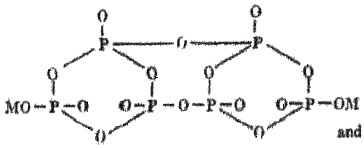
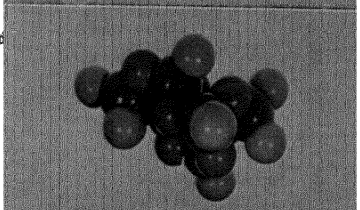
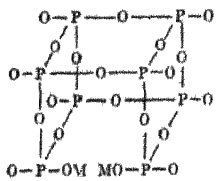
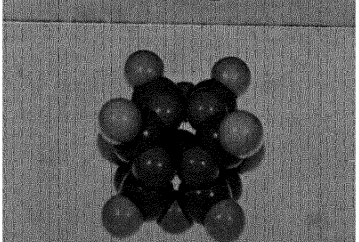
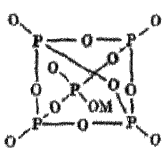
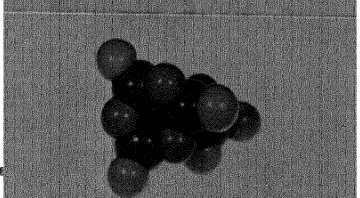
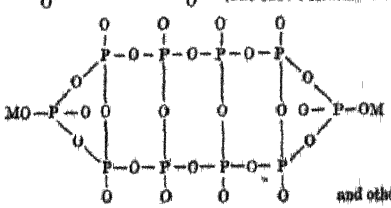
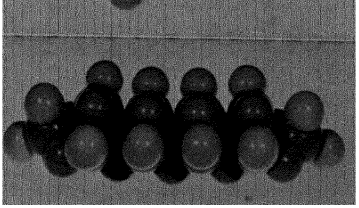
Formula		Spacial Representation
	$\frac{M_2O}{P_2O_5} = 4/5 = 0.800$ $M_8P_{10}O_{29}$ and others	
	$\frac{M_2O}{P_2O_5} = 3/4 = 0.750$ $M_6P_8O_{23}$	
or 		
or  and others		
	$\frac{M_2O}{P_2O_5} = 2/3 = 0.667$ $M_4P_6O_{17}$	
 and probably others		
	$\frac{M_2O}{P_2O_5} = 1/2 = 0.500$ $M_2P_4O_{11}$	

TABLE 11-5 (*continued*)

Formula	Special Representation
 $\frac{M_2O}{P_2O_5} = 3/7 = 0.429$ $M_3P_7O_{18}$ and others	
 $\frac{M_2O}{P_2O_5} = 1/3 = 0.333$ M P_3O_8 (A strained structure) or $M_3P_6O_{16}$ (The double formula which is not strained	
 and others	
$\frac{M_2O}{P_2O_5} = 1/4 = 0.250$ $M_2P_8O_{21}$  and others	
 $\frac{M_2O}{P_2O_5} = 1/5 = 0.200$ M P_5O_{13} (A strained structure) or $M_2P_{10}O_{26}$ (The double formula which is not strained	
 and others	

From the examples given in Table 11-6, a general formula for this family of ultraphosphates can be derived. This formula is

$$M_{(6+n)/3}P_nO_{(3+8n)/3} \tag{11-8}$$

where n is any multiple of 3 and is equal to the number of phosphorus atoms in the phosphate molecule-ion.

TABLE 11-6
Chemical Formulas for Individual Coupled-Ring Ultraphosphates
(See equation 11-7 for their structure)

Number of rings (x)	Formula	M_2O/P_2O_5 (R)
1	$M_3P_3O_9$	1:1
2	$M_4P_6O_{16}$	2:3
3	$M_5P_9O_{25}$	5 9
4	$M_6P_{12}O_{33}$ (not simplest form possible for $R = {}^1/_2$)	1:2
5	$M_7P_{15}O_{41}$	7:15
6	$M_8P_{18}O_{49}$	8·18 (4:9)
7	$M_9P_{21}O_{57}$	3 7
∞	MP_3O_8	1·3

This system may also be expressed in terms of the number of rings per structure. Let x represent the number of rings in each such phosphate molecule-ion; then

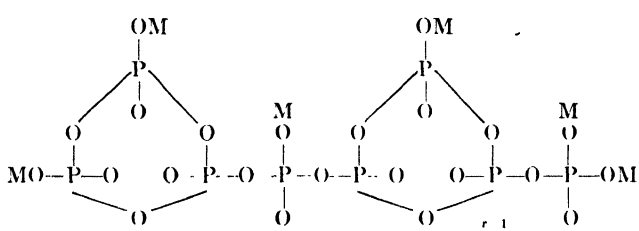
$$M_{x+2}P_{3x}O_{8x+1} \tag{11-9}$$

is a general formula for this kind of regular ultraphosphate. As the number of rings becomes infinite

$$\lim_{x\to\infty} M_{x+2}P_{3x}O_{8+1} = (MP_3O_8)_x \tag{11-10}$$

and the M_2O/P_2O_5 ratio $= {}^1/_3$ for the infinite structure.

Another hypothetical system may be formed in which the trimetaphosphate rings are connected by an O—P—O bridge, as shown below:



(11-11)

This structure may be treated in the same way as was the preceding one to get a general formula in terms of the number of phosphorus atoms. This formula is

$$M_{(n+4)/2}P_nO_{(11n+4)/4} \tag{11-12}$$

where n is any multiple of four. Expressing this in terms of the number of trimetaposphate rings, the formula is

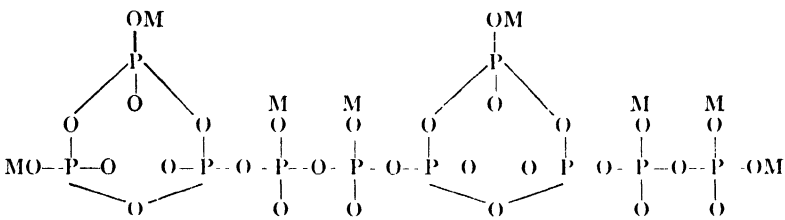
$$M_{2x+2}P_{4x}O_{11x+1} \tag{11-13}$$

and

$$\lim_{x\to\infty} M_{2x+2}P_{4x}O_{11x+1} = (M_2P_4O_{11})_x \tag{11-14}$$

giving $M_2O/P_2O_5 = 1/2$ for the infinite structure.

A more complicated hypothetical structural system may be formed from trimeta rings and two-membered chains.



(11-15)

The general formula in terms of phosphorus atoms

$$M_{(3n+10)/5}P_nO_{(14n+5)/5} \tag{11-16}$$

and in terms of rings is:

$$M_{3x+2}P_{5x}O_{14x+1} \tag{11-17}$$

The limiting case is

$$\lim_{x\to\infty} M_{3x+2}P_{5x}O_{14x+1} = (M_3P_5O_{14}) \tag{11-18}$$

Therefore, the limiting M_2O–P_2O_5 ratio is $M_2O/P_2O_5 = 3/5$. These results may be generalized for singly linked trimeta rings and N-membered chains. Let x equal the number of rings in the structure.

N	General formula
0	$M_{x+2}P_{3x}O_{8x+1}$
1	$M_{2x+2}P_{4x}O_{11x+1}$
2	$M_{3x+2}P_{5x}O_{14x+1}$

The general over-all formula is then obviously the following:

$$M_{(N+1)x+2}P_{(N+3)x}O_{(4N+8)x+1} \tag{11-19}$$

and

$$\lim_{x \to \infty} M_{(N+1)x+2}P_{(N+3)}O_{(3N+8)x+1} = M_{N+1}P_{N+3}O_{3N+8} \tag{11-20}$$

and

$$\lim_{N \to \infty} M_{N+1}P_{N+3}O_{3N+8} = (MPO_3)_N \tag{11-21}$$

Thus, the limiting composition corresponding to an infinite number of rings connected together by chains of infinite length is the metaphosphate composition. This one example shows that the metaphosphate composition is a limiting case for some ultraphosphate families of compounds, as well as for the polyphosphate family (see equation 8-9 on p. 433).

The formulas given in equations 11-8, 11-12, 11-16, and 11-19 are isolated hypothetical examples of the host of families of molecule-ions with systematically repeating structures to be found in the ultraphosphate region of composition. An amusing task for a rainy afternoon is to derive chemical formulas for the various ultraphosphate systems of compounds which can be imagined. A more difficult task will be to synthesize them in the laboratory and to prove their structures.

CHAPTER 12

Amorphous Phosphates, Including Phosphate Glasses, Condensed Phosphoric Acids, and Phosphate Esters

INTRODUCTION AND HISTORY

The amorphous phosphates are of three major types: liquids, glasses, and the as-yet-unspecified materials which appear at temperatures quite far below the melting point during the thermal conversion of one crystalline phosphate into another. The unspecified materials are probably acidic glasses but could be finely divided amorphous substances, similar to carbon black. An example of such materials is presented on pages 642–648.

In this chapter the emphasis will be placed on liquid phosphates and glasses obtained by cooling certain of these liquids. Such liquid phosphates have been known for many years. In 1816 Berzelius[1] wrote about amorphous phosphoric acids which range from viscous liquids to materials which must be called either glasses or unusually rigid liquids at room temperature. Seventeen years later, Thomas Graham[2] described the vitreous sodium phosphate exhibiting the metaphosphate composition ($Na_2O/P_2O_5 = 1$). Since the time of Graham, the literature has contained numerous discussions of liquid or vitreous condensed phosphates. In a large part of this literature, however, the authors tried to interpret proximate chemical analyses in terms of one or two definite compounds, as they did not appreciate that amorphous substances often consist of a complex mixture of related compounds.

Liquids and Their Structure

By definition, a liquid* is a material which exhibits a definite volume but no particular shape, taking the shape of its container. The volume of a

[1] J. J. Berzelius, *Ann. Physik*, **53**, 393 (1816).

[2] T. Graham, *Phil. Trans.*, **123**, 253 (1833).

* Some rheologists use the term "liquid" to mean only those fluid substances, other than gases, which exhibit Newtonian viscosity. For the general liquid they use the term "fluid." This, however, is poor notation, since there is then no differentiation between gases and fixed-volume fluids (better known as liquids).

given amount of liquid is fixed at any temperature and/or pressure and does not change greatly with variation of either temperature or pressure. In general, the atoms in a liquid may be more or less associated together into polyatomic assemblages. Such assemblages may be molecules or molecule-ions which are held together by primary chemical bonds, or they may be agglomerates formed by association of the constituent atoms, molecules, or ions through secondary bonding, such as hydrogen bonds, Van der Waal's forces, or Coulombic attraction. Physical measurements on liquids show up association but are often not consistent and never clearly distinguish between the chemist's classifications as to types of association. For example, degrees of association, x, ranging from less than one up to practically infinity can be obtained for $(H_2O)_x$, using different methods of studying pure liquid water and water as a solvent or solute.

When a sharp differentiation is needed between primary and secondary bonds, one usually turns to the chemistry of carbon and its compounds. In organic chemistry, where there is little doubt as to what are molecules, it is found that in some liquids the parts of a given molecule exchange places with similar parts of other molecules, so that the molecular structures are continuously reorganizing. Examples of such redistribution reactions[3] appear in exchange of hydrogens[4] between the hydrocarbons and exchange of hydrogens between —OH groups of mixed alcohols, the latter being catalyzed by hydrogen ion. Another interesting exchange is between substituents on benzene rings, as in the formation of toluene in a mixture of xylene and benzene. Mixtures of anhydrides of organic acids are also found to give mixed anhydrides; and mixtures of organic acids with acid anhydrides come to equilibrium so that, if one organic acid is mixed with the anhydride of another, both acids appear in the anhydride form and in the acid form. The reorganization of molecular structures is also found in ester interchange,[3,5] which is sometimes called a displacement reaction. An example of this would be found in a mixture of ethyl acetate and methyl butyrate forming some methyl acetate and ethyl butyrate. Polyesters, when melted, undergo reorganization,[5,6] so that, if a sharp fraction of a

[3] G. Calingaert and H. A. Beatty, *Organic Chemistry*, ed. H. Gilman, 2nd ed., John Wiley & Sons, Inc., New York, 1943, Vol. II, Chapt. 24, pp. 1806–20.

[4] For example, M. D. Kamen, *Radioactive Tracers in Biology*, Academic Press, New York, 1947, pp. 138–47; D. B. Melville, *The Use of Isotopes in Biology and Medicine*, University of Wisconsin Press, Madison, Wis., 1948, pp. 164–67.

[5] R. C. Fuson, *Advanced Organic Chemistry*, John Wiley & Sons, Inc., New York, 1950, pp. 201 (ester interchange), 582 (Jacobsen reaction), and 606 (polyesters).

[6] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, pp. 12–25, 87–91, 320–21, 339, 347.

long chain polyester is melted with a sharp fraction of a short chain polyester, an intermediate, rather broad distribution of molecular weights is obtained. The mathematics of this process has been worked out by Flory.[6,7]

From the examples given above, it appears that in mobile condensed phases, the so-called secondary bonding often competes with the primary bonds. This means that liquids might be classified as to the rate at which the agglomerates form and break up. Naturally, such a classification would have to take account of the mechanism of the interchange process.

The closest analogs in organic chemistry to the condensed phosphates are the acid anhydrides and esters. Since these organic materials undergo reorganization when molten (in the liquid state), it should be expected that this would be the case with molten or liquid phosphates; and, indeed it is. As will be shown later in this chapter, nearly all of the evidence which demonstrates that the condensed phosphates reorganize in molten form has been developed for condensed sodium phosphates and phosphoric acids. It is also believed that a similar but less rapid reorganization takes place in the esters of condensed phosphoric acids, with the rate of making and breaking of P--O – P linkages being faster than that of C—O--P linkages. However, experiments designed to show random reorganization or its effects have not as yet been carried out with the esters of condensed phosphoric acids, primarily because of the slow rate of exchange (see p. 584).

Glasses and Their Structure

By definition, a solid is a material which exhibits a definite volume and keeps its shape. As is the case with liquids, the density of a solid does not change greatly with variations in temperature or pressure. In general, homogeneous solids tend to be either quite rigid or quite flexible. Rigid, homogeneous, single-phase solids (which deform only slightly, even when subjected to large shearing stresses) can be divided into the class of crystals and that of glasses. The flexible, homogeneous solids (which are readily deformed and undergo large deformations before breaking) are usually called elastomers. Properties of crystals such as hardness, rate of growth, rate of dissolution, and sometimes refractive index depend on direction; and x-ray studies of crystals show that the atoms in them are arranged in a regular array. Glasses exhibit a degree of rigidity comparable to crystals but can be and, on a large scale, often are truly isotropic with respect to all

[7] P. J. Flory, *J. Am. Chem. Soc.*, **64**, 2205 (1942).

properties. X-ray studies indicate that the array of atoms in glasses possesses a high degree of randomness similar to that in liquids. Nonisotropic glasses are similar to nonisotropic liquids in that the anisotropy is attributable to some special cause—usually strong shearing stresses during cooling to give some alignment of the assemblages of associated atoms.

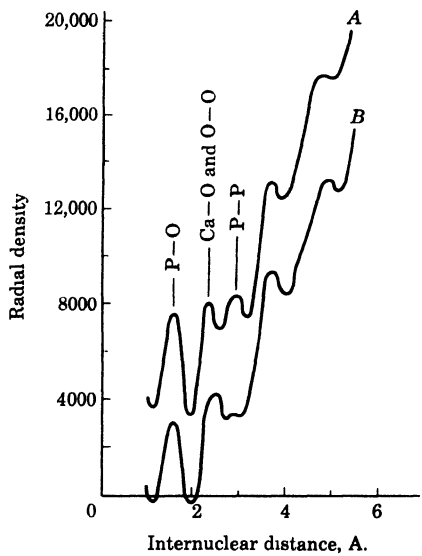


Fig. 12-1. Radial distribution curves for CaO–P_2O_5 glasses. Curves *A* and *B* are for CaO/P_2O_5 mole ratios of 0.731 and 0.964, respectively.

The only x-ray study of phosphate glasses which has appeared so far in the literature is an investigation of two calcium phosphate glasses on the ultraphosphate side of the metaphosphate composition, with the CaO/P_2O_5 mole ratios being equal to 0.731 and 0.964, respectively.[8] The radial distribution curves for these vitreous calcium phosphates are shown in Figure 12-1. The first peak in the radial distribution curves comes at 1.57 A. and is interpreted as representing the P-O distance in the glass. This distance indicates that in the glass the amount of π-bonding between the phosphorus and oxygen atoms is, on the average, nearly exactly $^1/_4$ π-bond per σ-bond. The measured area under this first peak in the radial

[8] J. Biscoe, A. G. Pincus, C. S. Smith, Jr., and B. E. Warren, *J. Am. Ceramic Soc.*, **24**, 116 (1941).

distribution curve corresponds to about 4.2 oxygens around each phosphorus atom for both glasses studied.

Within a regular PO_4 tetrahedron with a P-O distance of 1.57 A., the O-O distance must be equal to 2.56 A. In addition, the Ca-O distance should be about 2.4 A., according to the ionic radii (see Table 2-10). The second peak on the distribution curve occurring at 2.3–2.4 A. is therefore interpreted as the O-O and Ca-O peaks unresolved. Subtraction of the calculated area of the O-O peak from the over-all area of this measured peak indicates that there are about 6–8 oxygens surrounding each calcium atom. The third peak in the radial distribution function is stronger in the ultraphosphate glass for which CaO/P_2O_5 equals 0.731 than it is in the glass near the metaphosphate composition. This peak is attributed to the P-P distance. If the phosphorus atoms were diametrically opposite to each other, they would be separated by twice the P-O distance ($2d$ = 3.14 A.). The observed distance of 2.94 A. corresponds to an angle between the two oxygen bonds of about 140°. The greater intensity of this peak in the case of the glass for which CaO/P_2O_5 equals 0.731 is attributable to the fact that this glass exhibits 11% more P—O—P linkages than does the other glass.

According to most modern concepts, a glass is a liquid of extremely high viscosity in which the modes of molecular and/or atomic motion present in less viscous liquids are inhibited. There appears to be no rigorous way to differentiate a glass from a liquid without arbitrarily setting up artificial boundary values for viscosity and modulus of rigidity (shear modulus). During the last decade, it has been very clearly pointed out that some of the atomic modes of motion found in liquids are lacking in glasses.[9] Over a relatively restricted range of temperature (called the "glass transformation temperature") there is a sharp decrease in specific heat, thermal expansion, and compressibility as the temperature is lowered. This so-called "glass transformation" is caused by a relaxation effect, through which some process in the amorphous material occurs too slowly for thermodynamic equilibrium to be established in all degrees of freedom at low temperatures. Thus, a glass can be considered as a sluggish liquid, which is in what might be called a torpid state.

It now appears that the glass transformation temperatures are general rheological constants to which the temperature dependence of both viscous and elastic properties of liquids can be related.[10] Thus, although rapid

[9] For example, W. T. Kauzmann, *Chem. Revs.*, **43**, 219 (1948).

[10] For example, J. D. Ferry, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **16**, 91 (1955); also private communications of A. V. Tobolsky and T. G. Fox.

crystallization may prevent a given liquid from vitrifying, its glass transformation temperature can be estimated from its mechanical properties.

The problem of determining the detailed atomic or molecular arrangement in inorganic glasses has played an important role in glass science and technology. As might be expected, the literature on the subject is extensive; and there are a number of reviews[11] which clearly show the evolution of thought on this subject among scientists working in the field of glass technology. The picture of glass structure which has been generally accepted in the field of glass technology is a Zachariasen[12] random three-dimensional network of the glass-forming oxides (such as SiO_2 and P_2O_5) into which are scattered the counter-ions (Ca, Pb, Na, etc.). According to this qualitative picture of glass structure, the more counter-ions that appear in the glass, the less the three-dimensional network will be linked together. However, the entire structure is permeated by the network, and essentially all of the glass-forming oxides are tied into this network.

Very shortly after Zachariasen published his views concerning the structure of glass, Hägg[13] stated his belief that glasses were made up of large, irregular groups—with chain or sheet structures as possible, in the general case, as a three-dimensional network. As will be shown in the next two major sections of this chapter, in which a quantitative theory of glass structure is mathematically developed for the phosphates and is then compared with an impressive body of experimental data, the Hägg concept of glass structure is a reasonably good approximation to glasses corresponding to a rather wide range of composition, whereas the Zachariasen theory is a limiting case, truly applicable in the phosphate system only to vitreous P_2O_5.

REORGANIZATION THEORY[14,15]

Fundamental Ideas

As in Chapter 8, we shall let M stand for one equivalent of any cation or organic radical in a phosphate. Then reorganizing, single-phase liquid

[11] G. W. Morey, *Properties of Glass*, 2nd ed., Reinhold Publishing Corp., New York, 1954, Chapt. 20, pp. 548–71; J. M. Stevels, *Philips Tech. Rev.*, **8**, 231 (1946); E. J. Gooding and E. Meigh, *Scientific Foundations of Glass Manufacture*, ed. W. E. S. Turner, Society of Glass Technology, Sheffield, England, 1951, Vol. 2, Sect. A.

[12] W. H. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932); *J. Chem. Phys.*, **3**, 162 (1935).

[13] G. Hagg, *J. Chem. Phys.*, **3**, 42, 363 (1935).

[14] These general ideas on phosphates and inorganic glasses in general were first presented by J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 644 (1950).

[15] J. R. Parks and J. R. Van Wazer, *J. Am. Chem. Soc.*, **79**, 4890 (1957).

phosphates can be described in terms of an M_2O/P_2O_5 mole ratio. Although in high-temperature melts the oxygens of a given PO_4 group undoubtedly exchange positions with each other and with neighboring PO_4 groups, it is reasonable to expect that the phosphorus atoms are quite universally surrounded by four oxygen atoms and that, at any instant, a certain number of the PO_4 groups share oxygen atoms as demanded by the M_2O/P_2O_5 ratio. This means that the configuration of the phosphorus and oxygen atoms at any instant can be discussed in terms of the usual elementary structural units of phosphates: (1) isolated PO_4 units (ortho), (2) end units, (3) middle units, and (4) triple branching units. These units are shown on page 422. The quadruple branching unit described there is not considered here because such branching units are only found in heteropoly anionic structures or in mixed anhydrides in which an atom such as aluminum occurs within a tetrahedron of oxygen atoms—a tetrahedron which is essentially interchangeable with the PO_4 groups.

As was done in Chapter 8, we shall consider the structural units as including their accompanying M atoms, regardless of whether the M atom is bonded to the oxygen or is completely ionized. However, as will be shown later, the number and kind of condensed phosphate structures which can be found in a reorganizing liquid phosphate having a given composition are very dependent on whether there is a strong M—O bond or the M atom is ionized.

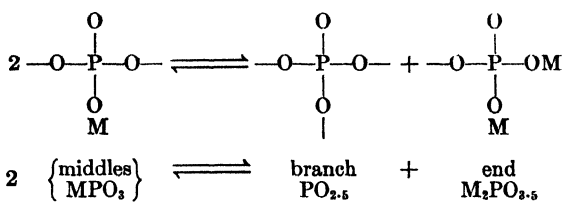
Following the ideas discussed on page 718, we shall assume that the molecule-ions of condensed phosphates in a single-phase liquid interchange parts by the making and breaking of P—O—P linkages. The first problem to be solved is to find the relative proportions of elementary structural units for any given M_2O/P_2O_5 ratio. Then, by using probability considerations, the structural units can be fitted together into molecules or molecule-ions of various sizes and shapes. In doing this, it should be remembered that branching units must connect through P—O—P linkages to three other PO_4 groups, with this set of three consisting of any combination of end units, middle units, and/or branching units. Likewise, middle units must connect to two other PO_4 groups, and end units to one other group. Orthophosphate (isolated PO_4 groups) and any unreacted M_2O that might be present cannot take part in building up a structure, although in the reorganization process these units can exchange their role and find a place in the various molecules or molecule-ions present in the single-phase liquid.

Naturally, the rate of reorganization does not enter into the considerations discussed here. The only requirement is that sufficient time shall have been allowed to elapse in order to achieve reorganization equilibrium.

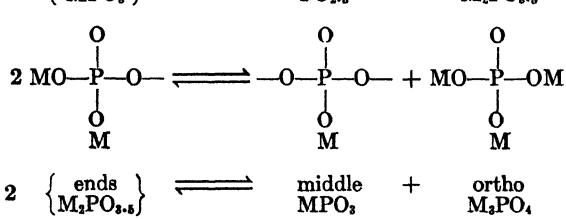
Although very little is definitely known about the time needed to achieve reorganization equilibrium, it is apparent that this time is related to the viscosity of the reorganizing phosphate and independently perhaps to the temperature as well, even though a temperature factor is included in the viscosity. Presumably, for liquid sodium or hydrogen phosphates having a viscosity around a poise, reorganization equilibrium is achieved in a rough order of magnitude of fractions of a second. However, in non-equilibrium glasses, in which the viscosities are greater than about 10^6 poises, it may take many centuries to achieve reorganization equilibrium; and, indeed, because of the freezing-in of various modes of motion, equilibrium may never truly be attained. As noted previously, the rate of breaking of C—O—P linkages in liquid phosphate esters is slow, although the P—O—P linkages probably make and break quite rapidly.

Exchange between Structural Units[15]

As exemplified by the following equations, structural units can react with each other so as to form different structural units. All of the combinations whereby structural units can react with each other to form different ones are given by equations 12-1 and 12-2 or can be obtained by adding or subtracting these two equations. Each equation is presented twice, first in expanded structural form and secondly in terms of the name and empirical composition of the structural units.



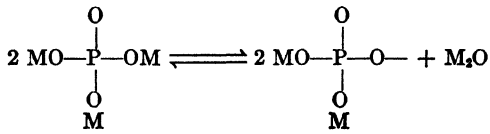
(12-1)



(12-2)

In addition, in order to be completely general, the possibility of unreacted or free M_2O must be considered. This possibility can be included in the system of equations showing how structural units react with each other by incorporating equation 12-3 with equations 12-1 and 12-2. Again, by

adding and subtracting equations 12-1 through 12-3 in various ways, one can obtain all of the different relationships for interchange of branching units, middle units, end units, orthophosphate groups, and unreacted M_2O.



(12-3)

Since the three equations given above represent equilibria, it is natural to think of them in terms of equilibrium constants. Such equilibrium constants, however, are rather unusual in that the quantities involved in them are parts of molecules or molecule-ions rather than the whole molecule or ion. However, we are discussing equilibrium between these structural units and therefore presuppose that the molecules or molecule-ions make and break many times during the period in which equilibrium is achieved. This means that, for the purposes of this discussion, the molecules or molecule-ions may be considered as unstable agglomerates having no more effect on the equilibria than association of water molecules through hydrogen bonding has on equilibria involving H_2O. The equilibrium constants corresponding to equations 12-1 through 12-3 are given below (with the counterions being included with each structural unit when the M atoms are ionized):

$$K_1 = be/m^2 \tag{12-4}$$

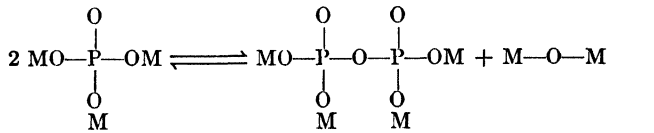
$$K_2 = mo/e^2 \tag{12-5}$$

$$K_3 = e^2u/o^2 \tag{12-6}$$

where b stands for the mole fraction of branching units, m for the mole fraction of middle units, e for the mole fraction of end units, o for the mole fraction of orthophosphate, and u for the mole fraction of unreacted M_2O.

The reaction shown in equation 12-3 is different from the reaction shown in 12-1 and 12-2 in that the formation of unreacted M_2O is not a basic property of reorganizing phosphates but depends on the relative free energies of the unreacted M_2O and the phosphate, $x\,M_2O \cdot y\,P_2O_5$. In other words, equation 12-3 will be shifted completely to the left except for those cases where M_2O is an extremely stable compound in itself. In a liquid where phosphates are reorganizing, it is quite probable that the unreacted M_2O will also reorganize. In such a case, it is not fair to write the equilibrium constant for equation 12-3 in the form given in equation 12-6. Rather,

the equation can be rewritten so as to cover molecular forms, as shown below:



(12-7)

$$K'_3 = (2e)u/o^2 \qquad (12\text{-}8)$$

Now the equilibrium shown in equation 12-7 should logically not be combined with the equilibria of equations 12-1 and 12-2, since these are different types of equilibria. In order to get all of the possible combinations, one could write a whole series of equations such as the one whereby orthophosphate reacts with pyrophosphate to give tripolyphosphate plus unreacted M_2O. To a first approximation, however, such a series of equations is probably unnecessary, since unreacted M_2O will undoubtedly occur only in the region where $R = M_2O/P_2O_5$ is large (near 3), and ortho- and pyrophosphates must predominate in this region. Therefore both K_3 and K'_3 should be tried in fitting these equations to experimental data, since the best representation (to the first-approximation theory given here) is probably achieved by gradually shifting from K'_3 to K_3 as R decreases.

We now have the problem of determining which of the four phosphate structural units will be found for a given value of the M_2O/P_2O_5 mole ratio, R, at reorganization equilibrium under any fixed set of circumstances. We also want to know in what relative proportion these structural units will appear. This information can be obtained by combining the equations for K_1, K_2, and K_3 or K'_3 with (1) an equation for R in terms of the structural units and (2) with a normalizing equation. Since an orthophosphate group has one P and three M's, an end group has one P and two M's, etc., R can be expressed in terms of the structural units as shown below in equation 12-9. The normalizing equation, 12-10, is based on the fact that the mole fractions of the various units must add up to unity.

$$R = M_2O/P_2O_5 = M/P = (3o + 2e + m + 2u)/(b + m + e + o) \qquad (12\text{-}9)$$

$$b + m + e + o + u = 1 \qquad (12\text{-}10)$$

We now have five unknowns (b, m, e, o, and u) and five equations in which there are three adjustable constants (K_1, K_2 and K_3 or K'_3) plus the com-

position parameter, R. This means that knowing K_1, K_2, and K_3, a solution can be obtained for the relative proportions of phosphate structural units as a function of R. The five equations have been solved by putting them in a parametric form so that the five unknowns and R are made functions of a single parameter.

In those cases where unreacted M_2O does not occur, the equations for K_3 or K'_3 are eliminated, and u is removed from equations 12-9 and 12-10. Then, we have four unknowns and four equations which are solved in exactly the same manner as when there were five unknowns and five equations. When there is no unreacted M_2O, there are only two adjustable constants.

Now, there is the problem of determining what *a priori* predictions can be made about the magnitude of the adjustable constants, K_1, K_2, and K_3 or K'_3. As previously stated, K_3 or K'_3 depends on the relative stabilities of the compound M_2O and the phosphate $x\,M_2O \cdot y\,P_2O_5$. Thus, where M stands for an alkali or alkaline earth metal, one would expect no unreacted M_2O, so that K_3 or K'_3 would be equal to zero, and unreacted M_2O would not play a role in any of the five equations which would then be reduced to four simultaneous equations This is probably approximately true where M_2O represents the oxide of any rather electropositive metal, including all of the transition metals. However, where M stands for hydrogen or for an organic radical, such as an alkyl group, K_3 or K'_3 should have a relatively high value, of the order of magnitude of 10^0–10^3. Probably the formation of ethers in the alcoholysis of trialkyl phosphates is an example of an approach to such an equilibrium.[16] In summation, it appears that in the case of phosphates having highly ionized counter ions, K_3 or K'_3 is zero, whereas, in the case of phosphates in which the M—O bond exhibits considerable covalent character, K_3 or K'_3 is apt to be a large number because, in such cases, the compound M_2O will be relatively stable with respect to reactions with liquid phosphates involving scission of P—O—P linkages to give P—O—M linkages

The values of K_1 and K_2 are very dependent on whether the M is ionized or is covalently bonded to the O. In the case of complete ionization of the M (no M—O bonds), orthophosphate ions, end, middles, and branching units correspond to PO_4 groups bearing 3, 2, 1, and 0 negative charges, respectively. This means that driving reactions 12-1 and 12-2 to the right converts two PO_4 groups having given charges into a group having a higher and a group having a lower charge, so that there would be high and low local concentrations of the counter-ions (M^+). Naturally, such local

[16] W. H. C. Rueggeberg and J. Chernack, *J. Am. Chem. Soc.*, **70**, 1802 (1948); A. D. F. Toy, *ibid.*, **66**, 499 (1944).

concentrations of counter-ions are highly improbable according to the standard fluctuation calculations of statistical mechanics,[17] so that the over-all equilibrium will correspond to equations 12-1 and 12-2 being strongly driven to the left. In other words, for completely ionized counter-ions, the tendency is to have as few phosphate building blocks as possible for any given value of R. Hence, the ideal case of the completely ionized M atom corresponds to the condition where $K_1 \rightarrow 0$, $K_2 \rightarrow 0$, and K_3 or $K'_3 = 0$. Where there is some slight tendency for formation of an M—O bond (a little covalent character), K_2 will take on a small value, say 10^{-2}. However, K_1 should be still smaller because of the Antibranching Rule discussed on pages 437–441. This means that, in reorganizing systems where the M atom is either completely or partially ionized, K_1 should always be a very small number, close to zero.

When there are strongly covalent M—O bonds, as in phosphate esters (where M is an alkyl or aryl radical), K_2 will probably be very close to 0.33, since there is no reason for the equilibrium to be driven to either the right or the left. On the other hand, K_1 will lie somewhere between zero and unity, perhaps about half way. For strongly covalent M—O bonds, the Antibranching Rule may not have much application, since even the PO_4 group in the orthophosphates becomes somewhat like a branching point, according to the hypothesis presented to explain the rapid hydrolysis of tetralkyl pyrophosphate on page 632.

The temperature dependence of the relative proportions of the various structural units at a given value of R depends on the variations of the equilibrium constants K_1, K_2, and K_3 or K'_3 with temperature. These, in turn, are controlled by the heats of the reactions described in equations 12-1, 12-2, and 12-3 or 12-7. In either the completely ionic or completely covalent case, the number of M—O and P—O bonds is the same on each side of either equation 12-1 or 12-2. And, furthermore, phosphate structures are involved in both sides of the equations. In other words, these equations correspond to what might be called isomerization reactions, the enthalpies of which are usually relatively small (no more than several kilocalories per mole). Therefore, the values of K_1 and K_2 will probably not change greatly with temperature. In the case of crystalline disodium phosphate,[18] a value of $\Delta H = +16.2$ kcal./mole of P at temperatures near 150°C. has been obtained for the reaction shown in equation 12-7, with the

[17] J. C. Slater, *Introduction to Chemical Physics*, McGraw-Hill Book Co., New York, 1939, Chapt. VII.

[18] For $2\ Na_2HPO_4(c) \longrightarrow Na_4P_2O_7(c) + H_2O(g)$, $\Delta H = +16.2$ kcal., according to *Natl. Bur. Stds. Circ. No.* 500.

free M_2O being H_2O. On the other hand, values of -4 to -6 kcal./mole of P have been found for the heat of hydrolysis of the pyrophosphate ion in dilute aqueous solution,[19] and values around -12 kcal./mole have been found for the hydrolysis of adenosine triphosphate in dilute aqueous solution.[20] The hydrolysis of pyrophosphate is a reverse of equation 12-7 for M_2O being H_2O in large excess, and the hydrolysis of adenosine triphosphate is related to 12-7. Obviously, the value of ΔH to be used in determining the temperature dependence of 12-3 or 12-7 is reasonably high, of the order of magnitude of 10 kcal./mole. However, change in the relative proportions of ortho, ends, middles, and branching units with temperature will be slight for those M_2O–P_2O_5 compositions in which the M is strongly ionized.

Now let us see how the distribution of structural units changes with the M_2O/P_2O_5 mole ratio, R, for various values of K_1 and K_2, assuming no unreacted M_2O (*i.e.*, K_3 or $K'_3 = 0$). The mole fraction of branching units, middle units, end units, and orthophosphate groups are presented in Figure 12-2 for values of R ranging from 0 to 3. In all cases, at $R = 0$ there is nothing but branching units, and at $R \geqslant 3$ all of the PO_4 groups are orthophosphates. In the completely ionic case where K_1 and K_2 are both equal to zero, there are three distinct regions of composition. In one of them for which R lies between zero and one, only branching and middle units are to be found. In the second region for which R lies between one and two, only middle units and end units are to be found. In the third region where R lies between two and three, only end units and orthophosphate ions should occur At the exact values of R equal to 0, 1, 2, and 3, only branching units, middle units, end units, and orthophosphate ions, respectively, are to be found. In the extreme covalent case, K_1 and K_2 are both equal to 0.33. This value corresponds to complete randomness, with the three ligand sites on a PO_4 group being indiscriminately satisfied by either an —M or a $—PO_3$. With $K_1 = K_2 = 0.33$, branches, middles, ends, and orthophosphate groups appear simultaneously for all values of R lying between 0 and 3.

It is conceivable that, when these ideas of exchange between structural units are applied to systems other than the phosphates, there may be cases where K_1 and K_2 are greater than 0.33. An example corresponding to $K_1 = K_2 = 0.8$ is given in Figure 12-2. Values of K_1 and K_2 larger than

[19] H. Giran, *Compt. rend.*, **135**, 961 (1902); N. S. Ging and J. M. Sturtevant, *J. Am. Chem. Soc.*, **76**, 2087 (1954).

[20] P. Ohlmeyer, *Z. Naturforsch.*, **1**, 30 (1946); O. Meyerhof and K. Lohmann, *Biochem. Z.*, **253**, 431 (1932).

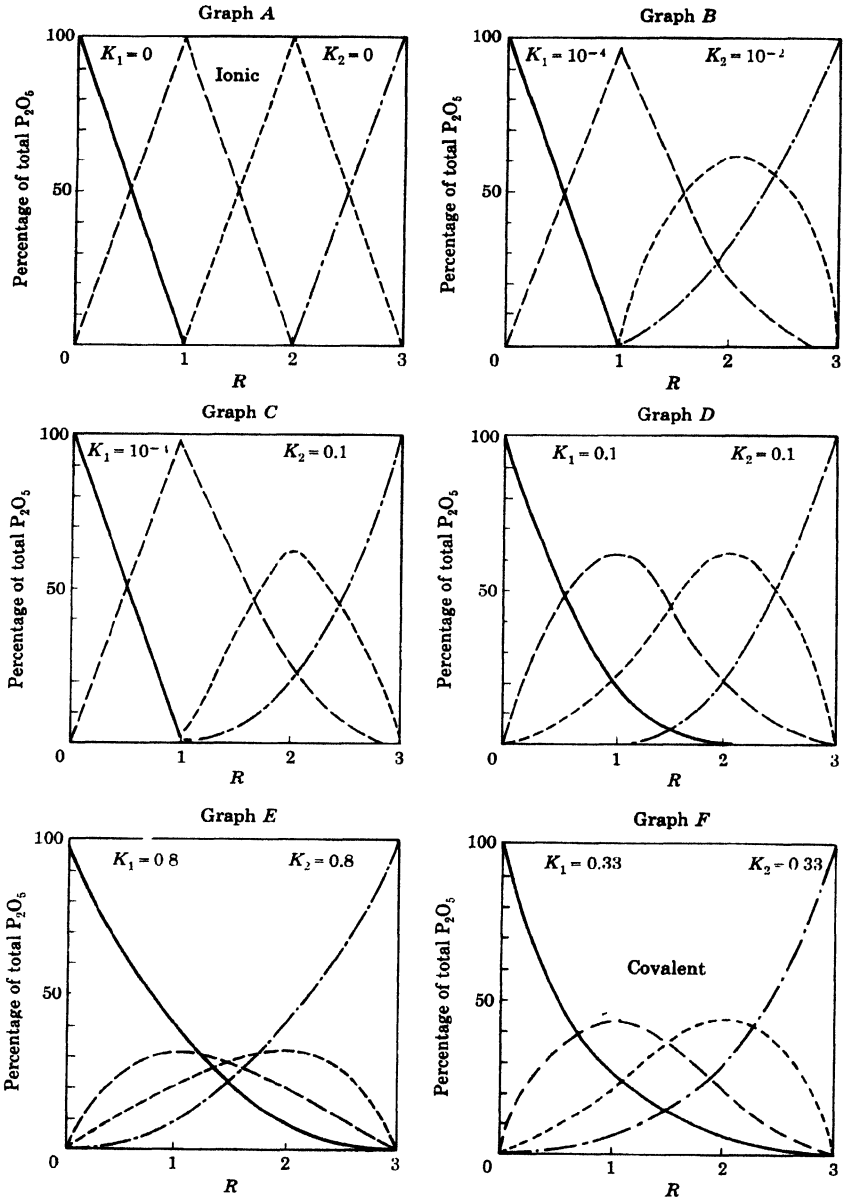


Fig. 12-2. Relative proportions of branching, middle, and end units as well as of orthophosphate as a function of the M_2O/P_2O_5 mole ratio, R, for various selected values of the equilibrium constants K_1 and K_2. There is no unreacted M_2O, as K_3 is set equal to zero. ———— Branch units; — — — middle units; — - — - ortho units; - - - - end units.

0.33 indicate that branching and isolated (ortho) groups are preferred. In the limiting case of $K_1 = K_2 = \infty$, the system will consist solely of an infinite network with interspersed ortho groups, for all values of R between 1 and 3.

In Figure 12-3, the distribution of structural units is shown for an imaginary case in which unreacted M_2O is allowed ($K_3 = 10$). By com-

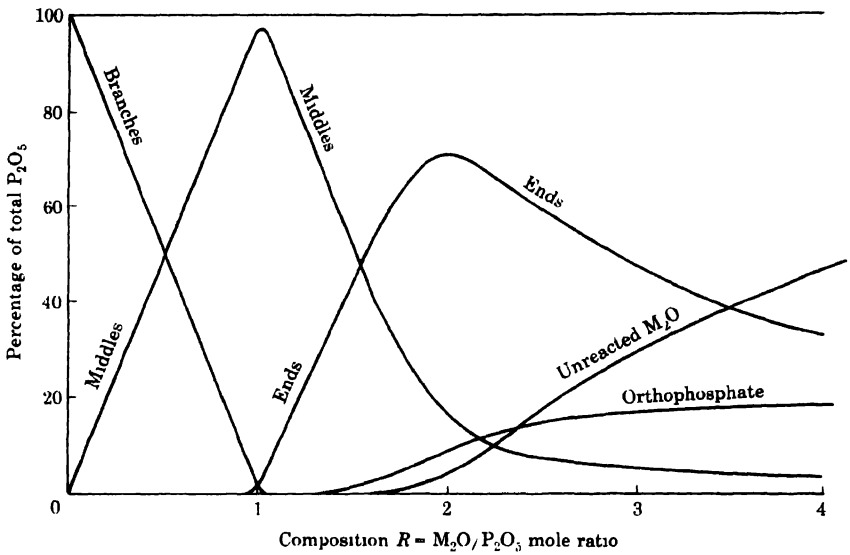


Fig. 12-3. A hypothetical curve showing relative proportions of branches, middles, ends, orthophosphate, and unreacted M_2O as a function of the M_2O/P_2O_5 mole ratio for $K_1 = 10^{-4}$, $K_2 = 2 \times 10^{-2}$, and $K_3 = 10$.

paring this figure with graph B of Figure 12-2, it can be seen that the curve showing orthophosphate concentration becomes very flat in the case where free M_2O is allowed, and it does not reach a maximum value at three, as is the case when there is free M_2O. Similarly, the concentration of end units does not go down to zero at $R = 3$ but still has an appreciable value at $R = 4$. It should be noted here that extension of the curves shown in Figure 12-2 (which depict the case of no unreacted M_2O) to values of R greater than three corresponds to a simple dilution of orthophosphate by M_2O. For R greater than three, there must necessarily be unreacted M_2O even when $K_3 = 0$, since the orthophosphate group can hold no more M atoms. In both Figures 12-2 and 12-3, the constant K_3 is employed instead of K'_3

in order to avoid unnecessary complications. However, in the experimental cases to be discussed later, it is necessary to use K's to get a close fit to the data.

Principles of Size Distribution

Knowing the relative proportions of the various structural units for any given value of R, we have the problem of putting these structural units together in a random manner so as to make molecules and/or molecule-ions Obviously, orthophosphate and unreacted M_2O are not involved in setting up structures, so that we are left with the problem of fitting together end units, middle units, and branching units by the same kind of random process that would occur in a reorganizing single-phase liquid.

If all of the structural units are ends, then only one kind of molecular structure can be made This is the pyrophosphate, which consists of two end units attached to each other If only middle units are present, ring structures of any size and/or infinitely long chains can form. On the other hand, if there are only branching units, the random structure will be a three-dimensional network similar to that described by Zachariasen,[12] with perhaps occasional cage structures, such as P_4O_{10} (see pp. 270–272), occurring in cavities of the network It is obvious that structures involving combinations of end units, middle units, and branching units will be hybrids of the three limiting cases described above. Since it was previously pointed out that, in the extreme ionic case, there should be only branching units at $R = 0$, only middle units at $R = 1$, only end units at $R = 2$, and only orthophosphate ions at $R = 3$, this special case is easy to visualize. A graphical interpretation of the structure as a function of the M_2O/P_2O_5 mole ratio, R, is shown for this case in Figure 12-4.

The factors determining the distribution of molecular structures which will result in a given phase undergoing reorganization at equilibrium are: (1) the kinds and relative amounts of structural units; (2) their functionality (ways they can be connected); (3) their geometry (atomic radii, etc.); (4) the geometry of how they are connected to each other (bond angles, etc.); and (5) the secondary interaction between the structural units (Van der Waal's forces, forces between atoms separated from each other by a number of other atoms in a molecule, etc.). Generally, a relatively good approximation[6] to the distribution found in a reorganizing system can be obtained by ignoring items 3 through 5 in the above list, and this practice will be followed in much of the discussion given below.

Following Flory,[6,7] we shall first treat the probabilities of connecting a branching unit to a branching unit, a branching unit to an end unit, and

an end unit to an end unit through various numbers of middle units. From these probabilities, a considerable amount of information can be derived about structures which should be found in reorganizing systems. In this treatment, however, ring structures (consisting of middle units only) are not included for two reasons: First, in a system in which structures are built up by adding structural units one at a time, no rings should form. This conclusion is based on a solution of the appropriate Random Walk

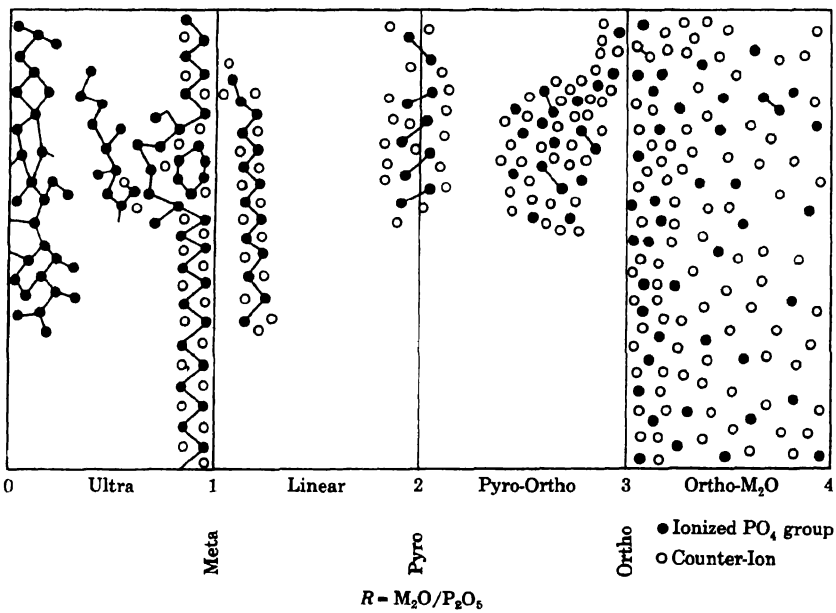


Fig. 12-4. Schematic structures as a function of composition for the ionic case

Problem.[21] Secondly, the stability and formation of rings is believed to be dependent to a considerable extent on the geometry of the structural units and the details of how they are connected (items 3 and 4 in the listing given in the preceding paragraph). Consideration of these factors makes the mathematics extremely complicated, so that middle units in any rings which are found in a practical experiment in organic polymer chemistry are considered as inactive and are not included in molecular size distributions which are compared with theoretical calculations.[6,7]

[21] H. Mark, *Physical Chemistry of High Polymers*, Interscience Publishers, New York, 1940, pp. 70–73.

In the approach, first employed by Flory, chain configurations are ignored. This is equivalent to making the tacit assumption that any and all configurations of the chains are possible. Such an assumption should be a good approximation to an un-ionized phosphate. The ionic case in which there are only end and middle units is then treated in terms of chains which are rigid rods.[15] This treatment takes into account the tendency of polyelectrolyte chains to extend to their full length because of the repulsion of the like charges along each chain.

There is a problem with respect to the stoichiometry of end units and branching units A middle unit can always be written as (MPO_3), but an end unit must be written as either (M_2PO_3) or (M_2PO_4) if fractional atoms are not allowed, and a branching unit must be considered as either a (PO_2) or (PO_3) if $(PO_{2.5})$ is disallowed. This problem can be overcome in two ways. First, it is possible to divide oxygens in half as has been done in the empirical formulas given in equations 12-1, 12-2, 12-3. On the other hand, one end of a chain can be considered as an (M_2PO_3) group and the other an (M_2PO_4) group, as indicated below.

$$\begin{array}{cccccc} O & O & O & O & \\ MOP & OP & OP & OPOM \\ O & O & O & O & \\ M & M & M & M & \\ e_1 & m & m & e_2 & \end{array} \qquad (12\text{-}11)$$

A similar treatment can be given for branching units. In developing the mathematical derivations of distribution functions for chain phosphates presented in this chapter, we have obtained solutions for both kinds of chains (those in which the ends are alike, and those in which the ends are different) and found that the distribution functions were the same in either case. Presumably, this is also true in the case of branching units, so that the way in which end and branching units are formulated, in terms of either whole numbers or fractions of atoms, is not pertinent to the problem of obtaining a proper molecular size distribution function.

General Random Reorganization Theory without Rings

In the general case, all five of the structural units will be present, with mole fractions b, m, e, o, and u. Since the orthophosphate and unreacted M_2O are regarded as diluents which do not serve as structural units and since end units must occur in pairs in molecular structures, the probabilities of branch, middle, and end units with respect to these building units themselves are given by the following equations:

$$\mathbf{b} = b/(1 - o - u - e/2) \tag{12-12}$$

$$\mathbf{m} = m/(1 - o - u - e/2) \tag{12-13}$$

$$\mathbf{e} = (e/2)/(1 - o - u - e/2) \tag{12-14}$$

Assuming a statistical equilibrium in the melt, we shall use the fundamental law of the probability of independent events, viz., the probability of a set of independent events. Thus, the probability that a branch unit is connected to a branch unit through i middle units is

$$P_{bbi} = \mathbf{m}^i\mathbf{b}^2/(\mathbf{b} + \mathbf{e}) \tag{12-15}$$

and the probability that a branch unit is connected to an end unit through j middle units is

$$P_{bej} = 2\mathbf{m}^j\mathbf{be}/(\mathbf{b} + \mathbf{e}) \tag{12-16}$$

This probability has a weight of two, since it covers connecting an end unit to a branching unit through intermediate middle units, as well as connecting a branching unit to an end unit through intermediate middle units. The probability of a linear chain molecule composed of k middle units and two ends is

$$P_{eek} = \mathbf{m}^k\mathbf{e}^2/(\mathbf{b} + \mathbf{e}) \tag{12-17}$$

It is of interest to know the value of the probabilities of these molecular forms regardless of the number of middle units composing the connecting chains. These probabilities are found by summing the above probabilities with respect to i, j, and k from 0 to ∞.

$$P_{bb} = \sum_{i=0}^{\infty} P_{bbi} = \frac{\mathbf{b}^2}{\mathbf{b} + \mathbf{e}} \times \frac{1}{1 - \mathbf{m}} = \frac{\mathbf{b}^2}{(\mathbf{b} + \mathbf{e})^2} \tag{12-18}$$

This is based on the following algebraic theorem

$$\sum_{x=0}^{\infty} a^x = \frac{1}{1 - a}$$

where $0 < a < 1$.

And similarly

$$P_{be} = 2\mathbf{be}/(\mathbf{b} + \mathbf{e})^2 \tag{12-19}$$

$$P_{ee} = \mathbf{e}^2/(\mathbf{b} + \mathbf{e})^2 \tag{12-20}$$

It should be noted that

$$P_{bb} + P_{be} + P_{ee} = 1 \tag{12-21}$$

This indicates that all the total possible forms have been counted. Equation 12-21 is to be used in discussing the population of linear chain molecules taken alone.

Equation 12-18 enables a criterion to be found which determines the composition, R, below which it is probable that infinitely branched structures may exist. In order for an infinitely branched structure to be found at values of R other than zero, the probability that a chain of middle units of any length chosen at random is connected to two other chains through a branch point must be greater than $^1/_2$. A set of N chains selected at random will, on the average, lead to $2NP_{bb}$ chains through branch points; and, for an infinitely branched structure to exist, the set of N chains must lead to a set of more than N chains. In order for this to be the case, the probability P_{bb} must satisfy the inequality

$$P_{bb} > {}^1/_2 \tag{12-22}$$

The inequality 12-22 combined with equation 12-18 yields the criterion that b and e must satisfy for the existence of an infinitely branched structure, namely:

$$\mathbf{b} > (1 + \sqrt{2})\mathbf{e} \approx 2.41\mathbf{e} \tag{12-23}$$

or

$$b > 1.21e \text{ by equations 12-12 and 12-14} \tag{12-24}$$

Infinitely or macrobranched, wall-to-wall structures are to be found in the composition range

$$0 \leqslant R < (3o + 2e + m + 2u)/(2.21e + m + o) \text{ when } b > 0. \tag{12-25}$$

When P_{bb} is exactly equal to $^1/_2$, the situation is indeterminate, inasmuch as no definite statement can be made as to whether an infinitely branched structure will exist or not. It is a certainty, however, that when $P_{bb} < {}^1/_2$, an infinitely branched structure is not possible. In this case, the branching units and some of the end units are used up in the production of branched molecules of finite size. When end units are present with middle and branching units, the above equations show that regardless of the value of P_{bb}, there will be a population of linear chain molecules also present in the structure of the system. Ignoring the Antibranching Rule, the general picture is that, for $P_{bb} < {}^1/_2$, there will be a mixture of branched molecular structures of finite size, linear structures, as well as orthophosphate and

unreacted M_2O. For $P_{bb} > 1/2$, an infinitely branched structure (three-dimensional network) occurs with branched and linear structures, orthophosphate, and unreacted M_2O filling the interstices of the network. It should be noted that, as the relative proportion of middle units increases, the infinitely branched network structure loosens, but not in the sense that Zachariasen[12] postulated for the loosening of the infinite structure of his ionic "glass-forming" network as the proportion of "glass-modifying" oxide (Na_2O, CaO) is increased.

Returning to the general case, it is seen that the distribution of the linear molecules among themselves is found by dividing equation 12-17 by a term based on equation 12-21.

$$1 - P_{bb} - P_{be} = \mathbf{e}^2/(\mathbf{b} + \mathbf{e})^2 \tag{12-26}$$

which gives the relative probability of a linear molecule with k middle groups as

$$P_k' = (\mathbf{b} + \mathbf{e})\mathbf{m}^k \tag{12-27}$$

That this is a proper distribution function is shown by the fact that unity results when P_k' is summed for k from 0 to infinity.

The number-average number of middle groups that is characteristic of this distribution is

$$\bar{k} = (\mathbf{b} + \mathbf{e}) \sum_{k=0}^{\infty} k\mathbf{m}^k = \frac{(\mathbf{b} + \mathbf{e})\mathbf{m}}{(1 - \mathbf{m})^2} \tag{12-28}$$

This is based on the following algebraic theorem

$$\sum_{x=1}^{\infty} xa^{x-1} = \frac{1}{(1 - a)^2}$$

where $0 < a < 1$

Or

$$\bar{k} = \frac{\mathbf{m}}{1 - \mathbf{m}} \tag{12-29}$$

Equations 12-27 and 12-29 can be used to calculate the distribution function as the weight fraction of the phosphorus or of the total P_2O_5 combined in the linear chain molecules only. This function is given by equation 12-30.

$$w(k) = \frac{(k + 2)(\mathbf{b} + \mathbf{e})}{\bar{k} + 2} \mathbf{m}^k \qquad 2 \leqslant k \tag{12-30}$$

where $w(k)$ = the weight fraction of the total phosphorus occurring in chains having k middle units.

When the system is such that the branching and end units satisfy the criterion for the existence of an infinitely branched structure (equation 12-24), there is a strong analogy with the "gel" and "sol" structures found in organic polymer theory.[6,7] In this case, the "sol" is not only the collection of linear chain phosphates but also the orthophosphate and unreacted M_2O. In a situation of this type, it is of interest to know the weight fraction of total phosphorus that is contained in these lower molecular weight constituents. It can be shown that this weight fraction, w, is given by the following equation

$$w = \frac{(1 - o - u)e^2}{(1 - u)(b + e)^2} + \frac{o}{1 - u} = \frac{(1 - o - u)e^2}{(1 - u)(2b + e)^2} + \frac{o}{1 - u} \qquad (12\text{-}31)$$

It is also interesting to determine the average number of middle groups between branching units and between a branching unit and an end unit in the three-dimensional network structure (the "gel" structure). These average values are, respectively, given by equations 12-32 and 12-33

$$\bar{\imath} = \sum_{i=0}^{\infty} iP_{bbi} = \mathbf{mb}^2/(\mathbf{b} + \mathbf{e})^3 \qquad (12\text{-}32)$$

similarly

$$\bar{\jmath} = 2\mathbf{bem}/(\mathbf{b} + \mathbf{e})^3 \qquad (12\text{-}33)$$

As noted previously, only branching units and middle units are present in the region for which R lies between 0 and 1 in the case of melts in which the M atoms are completely ionized. In such a case, e, o, and u are all zero and R reduces to $m/(b + m)$. Under these conditions, the average number of middle units between branching units, $\bar{\imath}$, reduces to m/b.

The number-average number of phosphorus atoms in a mixture of different-sized phosphate molecules and/or molecule-ions can be related to the weight fractions of the various molecules or molecule-ions making up the mixture. If N is the total number of phosphate molecules and/or molecule-ions in an assemblage and N_n is the number of molecules having n phosphorus atoms per molecule, the probability, P_n, of molecules of the nth size is

$$P_n = N_n/N \qquad (12\text{-}34)$$

$$P_n = x_n\bar{n}/n \qquad (12\text{-}35)$$

where x_n is the fraction of the total phosphorus as the nth sized molecule and $\bar{n}$ is the number-average number of phosphorus atoms per molecular structure in the assemblage. Since equation 12-35 normalizes to unity, then

$$\sum_{n=1}^{\infty} x_n/n = 1/\bar{n} \tag{12-36}$$

Random Reorganization of Flexible Chains

The preceding discussion has dealt with the general case in which all of the structural units are present. An interesting special case is found where the mole fraction of branching units is zero for values of R greater than some minimum value. Such cases are illustrated in graphs A, B, and C of Figure 12-2. Above these values of R, ends and middles are the only structure-forming units, and the over-all liquid consists of a distribution of linear chain molecules with orthophosphate and unreacted M_2O as diluents. It should be noted that the configuration (stiff or coiled) of these chains does not enter into the factors considered in developing the distribution theory. This is equivalent to tacitly assuming that the chains are infinitely flexible and can lie in any conceivable configuration. The probabilities of the occurrence of middles and ends relative to each other, without regard to the orthophosphate and unreacted M_2O present, are given by equations 12-13 and 12-14, respectively; and the probability distribution is given by equation 12-27. For $b = 0$, this latter equation becomes

$$P_k' = \mathbf{e}\mathbf{m}^k \tag{12-37}$$

The number-average of middle phosphorus atoms is still given by equation 12-29, and the weight fraction distribution of the polyphosphates becomes

$$w(k) = \frac{(k+2)\mathbf{e}}{\bar{k}+2}\,\mathbf{m}^k \tag{12-38}$$

These equations can be put into a more useful form by observing that the total number, n, of phosphorus atoms in a molecular structure with k middles is

$$n = k + 2 \tag{12-39}$$

and

$$\bar{n} = \bar{k} + 2 = (2m/e) + 2 \tag{12-40}$$

Since the sum of the probabilities of ends and middles is unity, equation 12-29 related the probabilities of middles to the number-average of middles. Then equations 12-37 and 12-38 can be written in terms of n and $\bar{n}$ as equations 12-41 and 12-42, respectively.

$$P_n = \frac{1}{n-1}\left(\frac{\bar{n}-2}{\bar{n}-1}\right)^{n-2} \quad \text{for } n = 2, 3, 4, 5, \ldots \text{ and } \bar{n} \geqslant 2 \quad (12\text{-}41)$$

$$w(n) = \frac{n}{\bar{n}(\bar{n}-1)}\left(\frac{\bar{n}-2}{\bar{n}-1}\right)^{n-2} \quad \text{for } n = 2, 3, 4, 5, \ldots \text{ and } \bar{n} \geqslant 2 \quad (12\text{-}42)$$

Equation 12-42 gives the weight distribution of the phosphorus present in chains made up of two or more phosphorus atoms. Since it has been postulated that the mole fraction of branch structural units is zero, the total phosphorus is distributed between the ortho and the chain population in the ratio

$$\frac{o/(1-u)}{1-[o/(1-u)]} \quad (12\text{-}43)$$

Hence, the weight fractions of the total phosphorus contained in the various molecular sizes are given by equation 12-44, assuming no rings.

$$w(n) = \frac{n}{\bar{n}(\bar{n}-1)}\left(\frac{\bar{n}-2}{\bar{n}-1}\right)^{n-2}\left(1-\frac{o}{1-u}\right) \quad \text{for } n = 2, 3, 4, 5, \ldots \text{ and } \bar{n} \geqslant 2 \quad (12\text{-}44)$$

This is called the flexible-chain distribution function.[14,15] The factor $o/(1-u)$ appearing in equation 12-44 is the fraction of total phosphorus present as the orthophosphate. Equation 12-44 meets the normalizing condition that the total phosphorus add up to unity, with rings ignored, since

$$\sum_{n=2}^{\infty} w(n) + o/(1-u) = 1 \quad (12\text{-}45)$$

The $\bar{n}$ appearing in equation 12-44 refers only to the chains for which the smallest allowed value of n is two. If the orthophosphate ($n = 1$) is included in the average, equation 12-36 can be employed to obtain the following equation for the number-average number of phosphorus atoms per molecule or molecule-ion:

$$\bar{n}' \text{ (including ortho)} = \frac{\bar{n}(1-u)}{o(\bar{n}-1)+(1-u)} \qquad (12\text{-}46)$$

where $2 \leqslant \bar{n} < \infty$ and $1 \leqslant \bar{n}'$ (including ortho) $< \infty$.

Reorganization of Rigid Rods[15]

The melts in which the M atoms are completely ionized represent an even more special case, in that there should be no orthophosphate or unreacted M_2O as well as no branching points in the region between $R = 1$ and $R = 2$. A distinguishing feature of this ionic case is that the number-average chain length, $\bar{n}$, is simply related to the composition variable, R. Examination of graph A in Figure 12-1 shows that the mole fraction of middle and end units is linearly related to R as follows.

$$m = 2 - R \qquad \text{for } 1 \leqslant R \leqslant 2 \qquad (12\text{-}47)$$

$$e = R - 1 \qquad \text{for } 1 \leqslant R \leqslant 2 \qquad (12\text{-}48)$$

Therefore, by equation 12-40

$$\bar{n} = 2/(R-1) \qquad \text{for } 1 \leqslant R \leqslant 2 \qquad (12\text{-}49)$$

Equation 12-49 may also be obtained from the definition of the composition parameter, R, as the ratio of the moles of M_2O to P_2O_5, and is, hence, also equal to the ratio of the number of atoms of M to atoms of P. If the structure is a distribution of chains only, then M is proportional to $\bar{n} + 2$, and P is proportional to $\bar{n}$, so that $R = (\bar{n}+2)/\bar{n}$. Solution of this equation for $\bar{n}$ in terms of R yields equation 12-49.

It is well known that uncharged polymer chains assume coiled configurations, whereas chain polyelectrolytes, in the absence of a swamping electrolyte, tend to be highly extended—approaching a rigid-rod configuration. Indeed, in flow birefringence measurements[22] on aqueous solutions of vitreous sodium phosphates, it was found that, the higher the concentration of the phosphate, the greater the alignment, so that measurable rotary diffusion constants could be obtained for glasses having average chain lengths, $\bar{n}$, as low as 10 when present in concentrated solutions (40% solution of the glass, $1.2\ Na_2O \cdot 1\ P_2O_5$). The effect whereby charged chain molecules prefer a stretched-out configuration can be explained, in the case of charges at fixed sites along the chain, by mutual repulsion of the charges or, in the case of mobile distributed charges, by a decrease in surface charge density due to increase in surface area on uncoiling.

[22] J. R. Van Wazer, M. Goldstein, and E. Farber, *J. Am. Chem. Soc.*, **75**, 1563 (1953).

If it is assumed that the molecule-ions in the wholly ionic case are thin, stiff rods, the liquid phosphates can be looked upon as a "brush heap" of molecule-ions, so to speak. This means that the ionized chain phosphates may be represented as line segments, the lengths of which are proportional to the number of phosphorus atoms, n, in the chain. Since the glassy state is considered isotropic, the vector sum of the segment lengths of the molecule-ions comprising the brush heap must be zero. Choosing the beginning or end of a particular molecule-ion as the head or tail of the vector will not cause trouble, since the choice is made randomly over a large population. The statistic that should be used to characterize the state is the square of the lengths of the segments. Analogously to the Maxwell-Boltzman law of the distribution of momentum in a perfect gas, the following equation can be written as the probability that a chain length, n, will lie between n and $n + dn$, regardless of its direction in the brush heap

$$dP_n = \frac{4\pi B n^2}{\pi^{3/2} A^3} \exp\left[-\frac{n^2}{A^2}\right] dn \qquad \text{for } n \geqslant 2 \tag{12-50}$$

The constant B is the normalizing factor, and A is proportional to the standard deviation of the distribution function which is proportional to the square root of the mean square lengths of the population of molecule-ions. The characteristic constants of this function can be determined by demanding that they satisfy simultaneously

$$\frac{4B}{\sqrt{\pi}\, A^3} \int_2^\infty n^2 \exp\left[-\frac{n^2}{A^2}\right] dn = 1 \tag{12-51}$$

and

$$\frac{4B}{\sqrt{\pi}\, A^3} \int_2^\infty n^3 \exp\left[-\frac{n^2}{A^2}\right] dn = \bar{n} \tag{12-52}$$

where $\bar{n}$ is calculated from the composition, R, by equation 12-49. The weight fraction corresponding to the chain length, n, is

$$w(n) = \frac{4B}{\sqrt{\pi}\, A^3 \bar{n}} \int_{n-1/2}^{n+1/2} n^3 \exp\left[-\frac{n^2}{A^2}\right] dn \qquad \text{for } n \geqslant 2. \tag{12-53}$$

The logical difficulties of applying a continuous function to an inherently discontinuous model are recognized. As has already been stated, no attempt is made here to use detailed information related to molecular structure as revealed by x-ray techniques. Thus far, the discussion also does not use the information regarding the fact that the average chain length is

determined by the relative probabilities of ends and middles for a given R. This information can be included by using an equation which defines the information content[23] of a molecule-ion, the probability of which is P_n.

The information content of a single molecule-ion lies in its structure and organization of its parts. The organization-information of the molecule-ions under discussion can be calculated from the assumption that they are simple one-dimensional arrays of parts, which are the ends and middles.[24] The information residing in the detailed structure, *i.e.*, bond angles, bond distances, etc., is in this instance being ignored, and the organization-information content of the molecule is, in the Shannon sense, the logarithm to the base 2 of the probability of the organization of the molecule. Inasmuch as random reorganization refers only to the organization of the molecule-ions, the probability of the organization of a molecule-ion containing $n - 2$ middle units in a population with a number-average chain length of $\bar{n}$ is given by equation 12-38 and the information content of such a molecule-ion is

$$I = -\log_2 \mathbf{e} - (n - 2) \log_2 \mathbf{m} \tag{12-54}$$

where

$$\mathbf{m} = (\bar{n} - 2)/(\bar{n} - 1) \tag{12-55}$$

and

$$\mathbf{e} = 1/(\bar{n} - 1) \tag{12-56}$$

Referring again to the concept of the glassy state in the ionic case—a brush heap of rod-like molecule-ions—a brush heap of information vectors can also be conceived. Equation 12-54 shows that the information content of the molecule-ion is a linear function of the number of phosphorus atoms making it up and, therefore, a function of its length; so that there is a one-to-one correspondence between the length of the molecule-ion and its information content. The information content may be considered to be a segment in information space possessing the orientation of the rod-like molecule-ion. In analogy to equation 12-50, the probability that a molecule-ion has information content between I and $I + dI$, regardless of orientation in the information space, is

$$dP = \frac{4BI^2}{\pi^{3/2}A^3} \exp\left[-I^2/A^2\right] dI \qquad \text{where } n \geqslant 2 \tag{12-57}$$

[23] A general reference on information theory is L. Brillouin, *Science and Information Theory*, Academic Press, New York, 1956.

[24] H. Jacobson, *Am. Scientist*, **43**, No. 1, 119 (1955).

in which B and A have the same significance as before. Since, by equation 12-53, this distribution function is a function of n, the constants for a particular value of $\bar{n}$ may be obtained by simultaneously solving the following equations:

$$\frac{4B}{\sqrt{\pi}\,A^3}\int_{-\log_2 \mathbf{e}}^{\infty} I^2 \exp\left[-\frac{I^2}{A^2}\right] dI = 1 \qquad (12\text{-}58)$$

$$\frac{4B}{\sqrt{\pi}\,A^3}\int_{-\log_2 \mathbf{e}}^{\infty} nI^2 \exp\left[-\frac{I^2}{A^2}\right] dI = \bar{n} \qquad (12\text{-}59)$$

With A and B so determined, the probability that the number of phosphorus atoms in a molecule-ion lies between n and $n + dn$ is

$$dP_n = \frac{-4B \log_2 \mathbf{m}}{\sqrt{\pi}\,A^3}\,[\log_2 \mathbf{e} + (n-2)\log_2 \mathbf{m}]^2 \exp\left[-\frac{[\log_2 \mathbf{e} + (n-2)\log_2 \mathbf{m}]^2}{A^2}\right] dn \qquad \text{for } n \geqslant 2 \quad (12\text{-}60)$$

and the weight fraction, $w(n)$, of total phosphorus in the molecule-ions containing n phosphorus atoms is

$$w(n) = \frac{-4B \log_2 m}{\sqrt{\pi}\,A^3 \bar{n}}\int_{n-1/2}^{n+1/2} n\,[\log_2 \mathbf{e} + (n-2)\log_2 \mathbf{m}]^2 \exp\left[-\frac{[\log_2 \mathbf{e} + (n-2)\log_2 \mathbf{m}]^2}{A^2}\right] dn \qquad \text{for } n \geqslant 2 \quad (12\text{-}61)$$

Equation 12-61 will be referred to as the rigid-rod distribution function describing the size distribution of randomly reorganizing, rod-like, highly ionized chain phosphates.

EXPERIMENTAL SIZE DISTRIBUTIONS COMPARED WITH THEORY

Determination of Size Distribution

As has been pointed out on pages 437–441, branching points are quickly degraded to end groups or middle groups in aqueous solution, according to the Antibranching Rule. Therefore, measurements in aqueous solutions are most readily interpreted for amorphous phosphates not containing branching points; and, indeed, only such compositions have as yet been carefully investigated. These compositions are the liquid phosphoric

acids for which the H_2O/P_2O_5 mole ratio is greater than unity, sodium, lithium, and potassium phosphate glasses for which Na_2O/P_2O_5 is greater than one, and some mixed sodium-hydrogen glasses for which $(Na_2O + H_2O)/P_2O_5$ is also larger than one.

Up to the present time, two procedures have been used to obtain reasonably accurate size-distribution data on aqueous solutions of amorphous phosphates. These two procedures are paper chromatography and solubility fractionation. For the lower molecular weight species ($1 \leqslant n <$ ca. 10 for chains, and $3 \leqslant n <$ ca. 8 for rings), paper chromatography gives a quite precise measure of the amount of the total P_2O_5 present as each individual size of chain or ring.[25] This technique has been applied to the study of amorphous phosphates primarily by Westman[26 29] and coworkers. It is not applicable to high molecular weight species because of the extremely small R_f values which would be involved (see pp. 702–703).

There are several methods (ion exchange chromatography and paper electrophoresis) related to paper chromatography which could be developed into useful tools for studying size distributions in amorphous phosphates. Of these methods, ion exchange chromatography probably offers the most promise.[30]

For long chain phosphates solubility fractionation, such as is used in studying organic high polymers,[31] gives a good separation into a series of overlapping fractions of decreasing chain lengths. The only procedure which has been described[32] so far for the solubility fractionation of phosphates consists of a stepwise addition of water-soluble organic compounds

[25] J. P. Ebel, *Bull. soc. chim. France*, **20**, 991 (1953), J. Crowther, *Anal. Chem.*, **26**, 1383 (1954); H. Grunze and E. Thilo, *Sitzber. deut. Akad. Wiss. Berlin, Kl. Math. u. allgem. Naturwiss.*, **5**, 1 (1953), revised in 1955; E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956).

[26] A. E. R. Westman and J. Crowther, *J. Am. Ceramic Soc.*, **37**, 420 (1954); also see H. Grunze, *Silikattechnik*, **7**, 134 (1956) and A. E. R. Westman and P. A. Gartaganis, *J. Am. Ceramic Soc.*, **40**, 293 (1957).

[27] A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956); also private communication from Prof. S. Ohashi of Kanazawa University, Japan.

[28] Private communication from A. E. R. Westman and P. A. Gartaganis. These investigators have found a possible source of error in their preparation of the sodium acid phosphate glasses and are now reinvestigating the system before publishing their work.

[29] A. E. R. Westman and P. A. Gartaganis, *J. Am. Ceramic Soc.*, **40**, 293(1957).

[30] J. Beukenkamp, W. Rieman, and S. Lindenbaum, *Anal. Chem.*, **26**, 505 (1954), J. A. Grande and J. Beukenkamp, *ibid.*, submitted for publication; J. P. Ebel and N Busch, *Compt. rend.*, **242**, 647 (1956).

[31] L. H. Cragg and H. Hammerschlag, *Chem. Revs.*, **39**, 79 (1946).

[32] J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 647 (1950)

(such as acetone) to a 5–10% aqueous solution of the phosphate, in order to precipitate small portions (about one-tenth) of the phosphate present in solution. Upon addition of the organic liquid, the phosphate solution becomes turbid; and an experienced operator can tell by the amount of turbidity approximately how much of the total phosphate has been precipitated in that fraction. The fraction is collected by centrifuging and comes out in the form of a small amount of a viscous oil. The first fractions, which represent the highest molecular weight material, are more viscous than the later ones.

The ring phosphates tend to congregate in the final fractions and predominate in the residuum left after fractionation. They can readily be distinguished from the chains by end-group titration or by fractional crystallization followed by a quantitative x-ray determination.

In addition to water-soluble organic liquids, the phosphates can be salted out of the solution by a number of ionic materials, including common table salt.[33] Also, polyvalent metal ions can be used to precipitate the phosphates fractionally. The barium precipitation method[34] can be made to act as a fractionating procedure by either having an excess of barium and increasing the pH in a stepwise manner or by adding the barium itself in small, successive portions to a mildly alkaline solution. In the latter case, it is advisable to add each portion of the barium at a moderately low pH and then to increase the pH in order to assure equilibrium precipitation of that fraction. Although the barium fractionation has been tested in a preliminary fashion,[33] it has never been developed into a good separation method because it appeared to offer no particular advantage. Organic amines,[35] cationic dyes,[35] and proteins[36] are also possible reagents for fractionating phosphates by precipitation.

It should be noted that fractionation merely separates a mixture into several less complicated mixtures which are called the fractions. Each fraction then should be classified by some method of measuring molecular weight. In the only published study of phosphate fractionation,[32] end-group titrations were employed to classify the fractions. Viscosity, diffusion, and other techniques could be used equally well.

Physical measurements in which moving boundaries are involved also yield information about size distributions of the diffusing substance. An

[33] J. R. Van Wazer, unpublished data.

[34] L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1947).

[35] J. P. Ebel, J. Colas, and N. Busch, *Bull. soc. chim. France*, **22**, 1087 (1955).

[36] B. J. Katchman and J. R. Van Wazer, *Biochim. et Biophys. Acta*, **14**, 445 (1954).

example of this is found in ultracentrifuge sedimentation[37] and in diffusion. Both techniques were used on a solution of a vitreous sodium phosphate (Graham's salt) to show qualitatively that there was a distribution of molecular weights.[38] This method of determining size distributions is capable only of giving an approximate answer, usually in the form of the spread of an assumed Gaussian distribution curve. As yet, no one has devised a quantitative method for measuring distributions of molecular size and/or shape in concentrated systems, such as a reorganizing phosphate, without dissolution in a solvent.

Composition of the Condensed Phosphoric Acids

In most of the early literature, the incorrect assumption was made that phosphoric acids, $x\,H_2O \cdot y\,P_2O_5$, in the region from $H_2O/P_2O_5 = 3$ to $H_2O/P_2O_5 = 0.7$ were mixtures of ortho-, pyro-, and metaphosphoric acids—with "pure" liquid pyrophosphoric acid occurring at $H_2O/P_2O_5 = 2$ and "pure" viscous metaphosphoric acid occurring in the range of $1.2 > H_2O/P_2O_5 > 0.7$. Indeed, several amorphous "metaphosphoric acids" which apparently only differed in their H_2O/P_2O_5 ratios have been described.

Probably Balareff[39] was the first person to understand clearly that the liquid condensed phosphoric acids consisted of mixtures of various phosphates, the proportions of which changed with the H_2O/P_2O_5 mole ratio. Following this author, several other studies[40,41] were made of the composition of strong phosphoric acids, but it was not until very recently—with the advent of paper chromatography—that really interpretable data have been obtained.[27] Unfortunately, the paper chromatographic procedure will not separate chain phosphates having more than nine or ten phosphorus atoms per chain, and therefore the composition of acids for which $H_2O/P_2O_5 >$ about 1.5 have not been completely determined, as shown by Table 12-1, in which the chromatographic data are presented.

It is interesting to note that liquid phosphoric acids of a given H_2O/P_2O_5 mole ratio appear to exhibit the same molecular composition regardless of their method of preparation and previous thermal history.[27] Furthermore,

[37] The theory of size-distribution calculations has been presented by N. Gralén, *Sedimentation and Diffusion Measurements on Cellulose and Cellulose Derivatives*, University of Uppsala, Uppsala, Sweden, 1944.

[38] O. Lamm and H. Malmgren, *Z. anorg. u. allgem. Chem.*, **245**, 103 (1940).

[39] D. Balareff, *Z anorg. Chem.*, **67**, 234 (1910); *ibid.*, **69**, 215 (1911).

[40] C. B. Durgin, J. H. Lum, and J. E. Malowan, *Trans. Am. Inst. Chem. Engrs.*, **33**, 643 (1937); *Chem. & Met. Eng.*, **44**, 221 (1937).

[41] R. N. Bell, *Ind. Eng. Chem.*, **40**, 1464 (1948).

TABLE 12-I

Molecular Composition of the Strong Phosphoric Acids Compared with the Theoretical Composition Calculated from the Flexible-Chain Model

Analysis				Percentage of Total P_2O_5 as																			
Wt-% P_2O_5	H_2O/P_2O_5 R	Overall n	$\bar{n}$ Corrected for unreacted H_2O	Ortho		Pyro		Tripoly		Tetrapoly		Pentapoly		Hexapoly		Heptapoly		Octapoly		Nonapoly		Higher	
				A*	B†	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
69.0	3 544	0 786	1 003	99 18		0 52																	
70 0	3 381	0 837	1 013	97 4		2 6																	
71 0	3 222	0 900	1 029	94 2		5 8																	
72 0	3 068	0 967	1 050	89 4		10 6																	
73 0	2 918	1 043	1 102	81 5		18 5																	
75 0	2 630	1 277	1 260	60 2		35 4	36 7	4 4	3 9		0 4												
76 2	2 462	1 368		49 2		42 0	43 1	8 4	7 2	0 4	1 1		0 1										
77 1	2 344	1 488		38 5		46 8	50 6	12 2	9 5	2 5	1 6		0 6										
78 3	2 192	1 678		28 0	-	49 1	47 7	16 5	16 3	5 2	4 7	1 2	1 3										
79 2	2 069	1 871	-	20 5	-	46 2	46 7	20 6	20 5	8 8	8 0	3 4	2 9	0 5	1 0								
80 1	1 960	2 083	-	15 4		39 1	40 4	24 4	22 9	12 7	11 5	5 7	5 4	2 3	2 5	0 5	1 1		0 5				
83 0	1 620	3 226	-	5 6		18 7	18 3	17 8	17 5	14 7	14 8	12 0	11 8	8 6	9 0	7 2	6 7	5 1	4 9	2 5	3 5	7 8	7 9
84.3	1 470	4 255	--	3 2	-	9 9	9 4	10 8	10 7	11 3	10 7	10 4	10 1	8 8	9 1	8.3	8 0	8 5	6 9	6 8	5 9	22 0	26 0
84 9	1 400	5 000	—	2 3		6 0	5 9	7 1	7 2	9 2	7 8	8 5	7 9	7 1	7 6	8 3	7 2	8 4	6 7	7 1	6 1	35 9	41.3
85 5	1 333	6 000	—	1 7		3 6	3 8	4 7	4 8	7 0	5 5	6 0	5 8	6 0	6 0	6 9	5 9	7 1	5 8	6 6	5 5	50 4	55.2
86 0	1 286	7 000	—	1 5	-	2 8	3 1	3 6	1 0	6 0	4 6	5 7	5 0	5 7	5 2	5 8	5 3	5 5	5.2	5 2	5 1	58 4	61 0
86 3	1 250	8 000	—	1 4		2 3	2 4	2 8	3 1	4 4	3 7	4 4	4 1	4 9	4 3	3 5	4 5	4 9	4 5	4 3	4 5	67 1	67 5
86 6	1 222	9 000	—	1 3	--	1 8	2 1	2 4	2 9	4 2	3 4	4 1	3 8	4 3	4 0	4 5	4 2	4.5	4 3	4 0	4 3	68 9	69.7

* A is the experimental value

† B is the theoretical value.

the chromatographic[27] and barium precipitation studies[41] show that ring phosphates are not present in detectable amounts in equilibrium acids for which the H_2O/P_2O_5 mole ratio is less than about 1.1. The question of the possible presence of branched phosphates cannot be directly answered by any of the studies reported thus far, because degradation at the branching points of randomly assembled molecule-ions containing branching units will lead to a distribution of variously sized chain phosphates (plus perhaps a few rings), and this distribution would be camouflaged by the expected distribution of variously sized chains.

Between 0 and about 69.0% P_2O_5 (below the theoretical analysis for H_3PO_4, which corresponds to 72.4% P_2O_5), the acids are found to be pure orthophosphates, and the properties of the various concentrations of orthophosphoric acid in this range are presented in Chapter 9. The first detectable amount of pyrophosphoric acid occurs at about 68.8% P_2O_5 ($H_2O/P_2O_5 \backsimeq 3.6$); and, at the composition corresponding to pure orthophosphoric acid, 72.4% P_2O_5 ($H_2O/P_2O_5 = 3.00$), there is 12.7% of pyrophosphoric acid. This means that, in the amorphous phosphoric acid having the composition of the pure ortho acid, there must be some free water to counterbalance the presence of pyrophosphoric acid. This is shown in Figure 9-2 in which the chromatographic analyses[27] on condensed phosphoric acids near the H_2O/P_2O_5 mole ratio of three are plotted to show the orthophosphoric acid, pyrophosphoric acid, and free water. The presence of free water in pure liquid sulfuric and nitric acids, as obtained by cryoscopic measurements, has also been reported.[42] Existence of free water in the liquid phosphoric acid for which $H_2O/P_2O_5 = 3$ is due to the action of equation 12-8. Application of this equation to the data of Figure 12-5 leads to the following equilibrium constant for the H_2O–P_2O_5 system:

$$K'_3 = \frac{(2e)u}{o^2} = \frac{[H_4P_2O_7][H_2O]}{[H_3PO_4]^2} = 0.020, \text{ based on mole fractions} \quad (12\text{-}62)$$

The mole fractions of free H_2O, orthophosphate, end units, and middle units were used to calculate the values of K_3 and K'_3 for the condensed phosphoric acids. These values are presented in Figure 12-5 from which it can be seen that K'_3 varies much less than does K_3 in the applicable range of the H_2O/P_2O_5 mole ratio, $2.4 < R < 3.3$. In Figure 12-6 the mole per cent of the total P_2O_5 present as the various structural units is compared with the theoretical curves obtained by setting $K'_3 = 0.02$, $K_2 = 0.08$, and $K_1 = 10^{-3}$. The value for K'_3 was chosen from Figure 12-5, and the

[42] R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, **1950**, 2473; *ibid.*, **1950**, 2552.

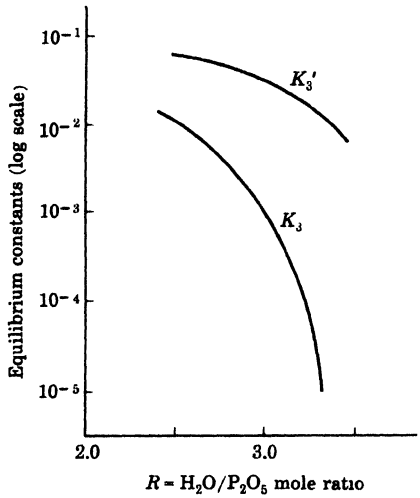


Fig. 12-5. Variation of the equilibrium constants for formation of unreacted H_2O in the condensed phosphoric acids.

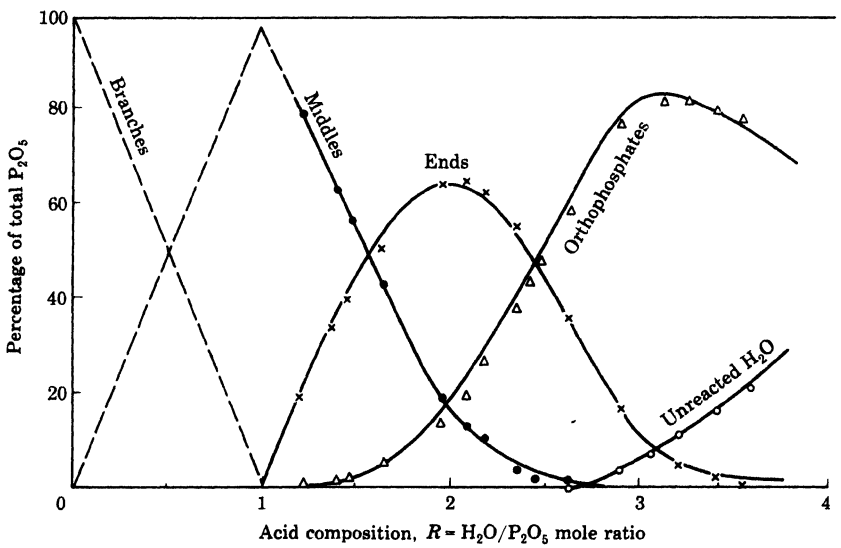


Fig. 12-6. Relative proportions of branching, middle, and end units as well as orthophosphate and free water as a function of the H_2O/P_2O_5 mole ratio. The smooth curves were calculated on the assumption of $K_1 = 10^{-3}$, $K_2 = 0.08$, and $K_3' = 0.02$.

value for K_1 was chosen from extrapolating the experimental data for middle units to $R = 1.00$. From the value of m at $R = 1.00$, it is simple to obtain a reasonably good approximation for K_1.

Since K'_3 is larger than zero, we can conclude that the H—O bonds in the water are roughly of the same order of magnitude both with respect to bond type and bond strength as the H—O bonds in the condensed phosphoric acids in concentrated form. Moreover, the fact that K_2 is reasonably large indicates that the hydrogens in the condensed phosphoric acids

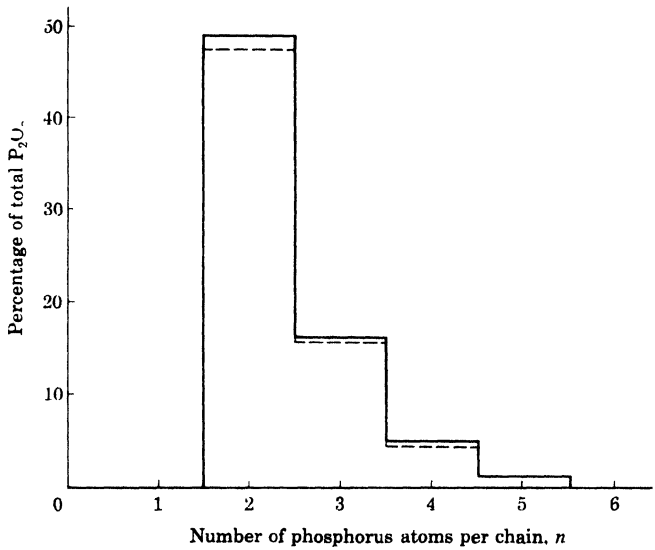


Fig. 12-7. Size distribution of chain phosphates in a condensed phosphoric acid for which $R = 2.192$, corresponding to 78.3% P_2O_5. ——— Experimental data (paper chromatography). - - - Calculated from the flexible-chain theory

in concentrated form are un-ionized to a considerable extent with respect to this criterion. If they were all ionized, it would be expected that the curve for c in Figure 12-6 would exhibit a maximum value of nearly 100% at $R = 2$. On the other hand, if the hydrogens were completely associated, the maximum at $R = 2$ would be only equivalent to about 45% of the total P_2O_5, instead of the observed value of 65%. Even though the analyses were carried out under conditions where branching units (if they were present) would be hydrolyzed and show up as end or middle units, it is still reasonable to believe that the data of Figure 12-6 give a reasonable

demonstration that the Antibranching Rule holds for the condensed phosphoric acids in concentrated form. This is so because the shape of the *m*, *e*, and *o* curve near $R = 2$ (a region where branching is not to be expected, except in the most extreme circumstances) corresponds to a value of K_1 which is close to zero ($\backsimeq 10^{-3}$). Since the curve for *m* in Figure 12-6 extrapolates up to only about 95% of the total P_2O_5 at $R = 1$, it would

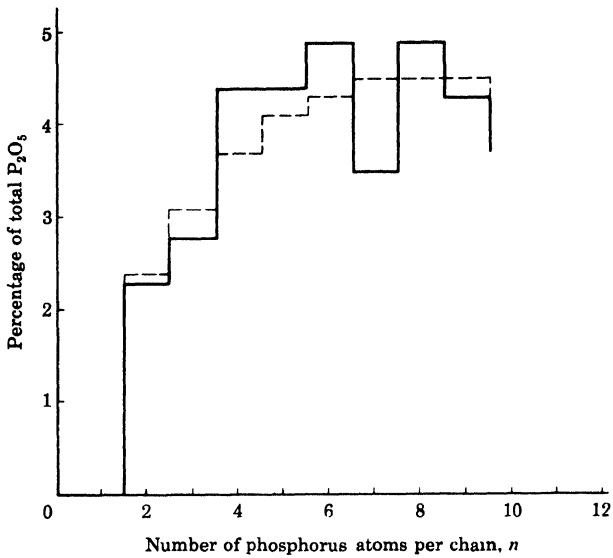


Fig. 12-8. Size distribution of chain phosphates in a condensed phosphoric acid for which $R = 1.286$, corresponding to 86.0% P_2O_5. ——— Experimental data (paper chromatography) - - - Calculated from the flexible-chain theory

appear that there is a small amount of branching for R larger than unity. It appears that about 2% of the total P_2O_5 is present as branching units at $R = 1.00$, but that there is an inappreciable amount at $R = 1.06$.

In Figures 12-7 and 12-8, the experimental size distribution is compared with the size distribution calculated on the basis of the flexible-chain model (see equation 12-44) for condensed phosphoric acids for which $R = 2.192$ and $R = 1.296$, respectively. It should be noted that the agreement between experiment and theory is excellent in both of these figures. For the condensed phosphoric acid of low molecular weight described in Figure 12-7, the rigid-rod model of the phosphate chain would give a considerably lower value for the pyrophosphate ($n = 2$) and would peak at the tripoly-

phosphate anion ($n = 3$). This model would also give moderately high proportions of molecular species corresponding to $n = 5$, 6, 7, and 8. Obviously, the rigid-rod model is a poor approximation to the distribution whereas the flexible-chain model fits the experimental data about as well as could probably be expected.

In Figure 12-8 there is obviously some experimental error, since it is very difficult to believe that the septapolyphosphate ($n = 7$) would be present in considerably lower amount than the hexapoly- or octapolyphosphate, as indicated by the chromatographic measurements. Again, the rigid-rod model would not give nearly as good a fit as is obtained with the flexible-chain model, since the distribution curve for the rigid-rod model would appear at much lower values of the per cent of total P_2O_5, as this model corresponds to a much flatter distribution, showing hardly any maximum.

For any given value of the H_2O/P_2O_5 mole ratio, it is possible to calculate the distribution of variously sized chains in the condensed phosphoric acids from equation 12-44 by relating $\bar{n}$ and $[o/(1-u)]$ to R. This has been done in the following equations in which the numerical constants are obtained empirically.

$$\left\{\begin{array}{ll} \bar{n} = \dfrac{2\left(1 - \dfrac{o}{1-u}\right)}{R - 1 - \dfrac{2o}{1-u}} & \text{for } 1.2 \leqslant R \leqslant 2.5 \qquad (12\text{-}63) \\ \bar{n} = 0.0216 - 0.0021(R - 2.500) & \text{for } 2.5 \leqslant R \leqslant 3.0 \qquad (12\text{-}64) \\ \bar{n} = 2 \quad \text{for } R > 3.0 & (12\text{-}65) \end{array}\right.$$

$$\left(\frac{o}{1-u}\right) = 0.44538 + 0.81060\,(R - 2.400) + 0.10843\,(R - 2.400)^2 - 0.50169\,(R - 2.400)^3 - 0.054292\,(R - 2.400)^4 + 0.15045\,(R - 2.400)^5 \quad \text{for } 1.2 \leqslant R \leqslant 3.6 \qquad (12\text{-}66)$$

Equation 12-66 was determined by the application of orthogonal polynomials.[43] By use of equations 12-66 and 12-44 along with the appropriate choice of equations 12-63, 12-64, or 12-65, the molecular constitution of any

[43] R. A. Fisher, *Contributions to Mathematical Statistics*, John Wiley & Sons, Inc., New York, 1950, Chapt. 3, pp. 119–26; R. A. Fisher and F. Yates, *Statistical Tables for Biological, Agricultural, and Medical Research*, 3rd ed., Hafner Publishing Co., New York, 1949.

condensed phosphoric acid for which $R > 1.2$ can be calculated more accurately than it can be determined from a single set of analyses, since equation 12-66 is based on a statistical treatment of a number of such analyses obtained over a range of values of R.

Effect of Dissolution on Sodium Phosphate Glasses

Some of the more reactionary adherents of the Zachariasen theory[12] of glass structure have questioned the structure theory presented in this chapter on the basis that measurements on solutions may not be at all pertinent to the structure of the solid before it was dissolved. This reasoning would, of course, normally occur to a person well versed in the technology of silicate glasses and knowing very little about phosphate glasses, since as pointed out on pages 446–449—the silicates readily rearrange and polymerize or depolymerize in aqueous solution. As is demonstrated in Chapters 8, 10, and 11, the chain and ring phosphates found in glasses for which R is greater than unity are quite stable in aqueous solution—only undergoing a slow hydrolytic degradation and never polymerizing under normal laboratory conditions (see p. 459).

In addition to the fact that unbranched phosphates—in contrast to silicates of any type—are, for all practical purposes, stable in aqueous solution, there is considerable evidence to indicate that the process of dissolution of a sodium phosphate glass for which $R > 1.0$ is not accompanied by appreciable changes in the kind and relative proportions of the phosphate molecule-ions. This is demonstrated by the fact that a given glass gives the same solution whether it is dissolved quickly (when a finely ground powder is added to violently agitated water in a Waring Blendor) or slowly (large chunks of glass added to water with occasional stirring so that dissolution would be completed in about 8 hr.). Furthermore, the same distribution of molecular species is found when the glass is dissolved in solutions of electrolytes as when it is dissolved in pure water. It is also found that the heat of dissolution of a phosphate glass for which $R > 1$ is of the order of magnitude to be expected for a simple process merely involving separation and hydration of the constituent molecule-ions and their accompanying cations. Thus, the heat of solution of a sodium phosphate glass for which $\bar{n} = 4.6$ is 9.9 kcal./mole of P_2O_5; and, for a glass for which $\bar{n}$ = about 230, it is 7.9 kcal./mole of P_2O_5. At the same concentration (1–3% dissolved salt), the heats of solution of anhydrous tetrasodium pyrophosphate and Forms I and II of sodium tripolyphosphate are 12.0, 10.7, and 9.4 kcal./

mole of P_2O_5, respectively. It should also be noted that the theory presented here predicts no orthophosphate in the sodium phosphate glasses. This is indeed found to be the case for their aqueous solutions, as is shown in Table 12-2. On the other hand, the dissolution of a Zachariasen network should give an appreciable proportion of orthophosphate, at least when the sodium phosphate glass is dissolved in sodium hydroxide solution.[26]

It should also be noted that solutions of sodium phosphate glasses for which $R > 1$ may be readily dehydrated in a vacuum at room temperature to give a horny, glass-like material which upon redissolution is found to exhibit essentially the same molecular composition. The term "horny, glass-like material" was used in the above sentence because it is very difficult to remove the last few per cent of water without heating to temperatures which would lead to hydrolysis followed by molecular recondensation due to dehydration. This small amount of water acts as a plasticizer, causing the resulting amorphous solid to be somewhat flexible and not so brittle as the original glass.

Some direct evidence has also been obtained to show that chain molecule-ions exist in solid phosphate glasses. The Raman and infrared spectra are most readily interpreted in terms of the same structures existing in solution.[44] Moreover, a recent study of the drawing of fibers from softened sodium phosphate glasses in the polyphosphate region of composition showed that the drawn glasses exhibited the type of x-ray diffraction pattern associated with oriented chain molecules.[45] It appears that the structural reorganization in the softening range of temperature is sufficiently slow so that the chain molecules can be oriented by pulling a fiber.

From the arguments presented here and the fact that crystalline chain and ring phosphates can be dissolved, recrystallized, and then redissolved without changing their anionic structure, it is apparent that measurements of the type, size, and proportions of molecule-ions present in solutions of the sodium phosphate glasses for which R is greater than unity give a clear picture of the structure of the undissolved glass. Obviously, the same statement applies to the condensed phosphoric acids and sodium acid phosphates for which $R >$ about 1.3; and most of the arguments given above apply to these materials. Of course, the argument dealing with lack of orthophosphate no longer applies to the amorphous acidic compositions, and it should be noted that unadjusted solutions of these materials tend to undergo much more rapid hydrolytic degradation due to their low natural pH.

[44] W. Bues and H. W. Gehrke, *Z. anorg. u. allgem. Chem.*, **288**, 291, 307 (1957).

[45] M. Goldstein and T. H. Davies, *J. Am. Ceramic Soc.*, **38**, 223 (1953).

Composition of the Sodium Phosphate Glasses

A series of sodium phosphate glasses can be quite readily made between the Na_2O/P_2O_5 mole ratios of 1.6 and 0. As described in the later section entitled Physical and Chemical Properties, the properties of the dissolved glasses undergo a considerable change at $R = 1.00$.* At this value, there are essentially no titratable end groups in the aqueous solution, which exhibits the physical properties of the solution of a reasonably high polymer. As R is decreased from 1.00, the solution becomes quite acidic, and the average molecular weight of the phosphate anions, as determined by any method, is found to decrease quite rapidly with time toward moderately low limiting values. On the other hand, as R is increased from 1.00, the average molecular weight of the phosphates in solution is found to diminish, but the solutions are quite stable with respect to continuing degradation and remain at a neutral or somewhat alkaline pH—depending on the amount of residual H_2O in the glass. All of this physical information is in accord with the idea that the sodium phosphate glasses exhibit a distribution of end, middle, and branching units corresponding to the completely ionic case, where K_1 and K_2 each equal zero. Furthermore, it is believed that K_3 or K_3' also equals zero, although no experimental evidence is available, since no one has studied glasses for which $R > 1.7$. The reason that glasses corresponding to the larger values of R have not been investigated is that crystallization occurs very rapidly in this region, so that it is impossible to prepare clear glasses by standard techniques. Some experiments have recently been carried out by Westman *et al.* on the preparation of glasses for which $R = 2$ in a special furnace in which the glasses are quenched practically instantaneously. From the preliminary reports,[46] it appears that the quenching follows the melting so rapidly in this furnace that reorganization equilibrium is not reached.

In Table 12-2 the distribution of molecular species ranging from $n = 2$ to $n = 9$ is plotted in such a way that the data obtained by paper chromatography[26,46] on a series of glasses for which $\bar{n}$ goes from 2.0 to 9.0 is compared with the theoretical values calculated from equation 12-61. In Figure 12-9 the chromatographic results on a glass having a composition equivalent to tripolyphosphate are compared with the results obtained from the distribution function of equation 12-61 based on the rigid-rod model of a phosphate chain. It should be noted that the fit between theory and experiment is

* In computing the value of R, it is necessary to include trace amounts of water which may be left in the glass from its preparation. Thus, R is equal to $(Na_2O + H_2O)/P_2O_5$, with $Na_2O \gg H_2O$.

[46] A. E. R. Westman, private communication.

TABLE 12-2

Molecular Composition of the Sodium Phosphate Glasses Compared with the Theoretical Composition Calculated from the Rigid-Rod Model

Analysis			Percentage of total P_2O_5 as																			
Wt.-%	Na_2O/P_2O_5		Ortho		Pyro		Tripoly		Tetrapoly		Pentapoly		Hexapoly		Heptapoly		Octapoly		Nonapoly		Higher	
P_2O_5	R	$\bar{n}$	A*	B†	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
53.383	2 00000	2 0	0 00	0 00	100 0																	
54.803	1 88888	2.25	0 00	0 00	91 81		8 19															
55.994	1 80000	2 5	0.00	0 00	72 24		27 76															
57.007	1 72727	2.75	0.00	0 00	47 03	28 94	52 13	55 34	0 84	14 84		0 86		0 02								
57.881	1.66667	3.0	0 00	0 00	24 32	21 0	48 55	44 1	20 41	27 2	5 11	6 7	1 61	0 8		0 2						
59.308	1.57143	3.5	0.00	0 00	11.13	13 73	38 27	26 83	28 11	28 26	13 12	18 91	5 52	8 63	2 33	2 83	1 02	0 67	0 48	0 11		0.03
60.426	1 50000	4.0	0 00	0 00	6 65	10.03	28 25	18 06	27 43	21 96	16 87	20 11	9 41	14 54	5 70	8 56	2 74	4 18	1 77	1 72	1 16	0 84
61.324	1 44444	4 5	0.00	0 00	4 74	7 74	22 17	13 15	23 99	16 81	17 30	17 51	11 52	15 46	8 24	11 85	4 60	7 99	3 15	4 77	4 29	4 72
62.063	1 40000	5.0	0.00	0 00	3 24	6.21	16.24	10 12	20 16	13 15	16 45	14 59	12 68	14 27	9.43	12 53	6 71	10 01	4 39	7 35	10.69	11.77
62.681	1.36364	5.5	0 00	0 00	2 65	5 06	13 94	8 09	19 14	10 57	17 92	12 14	14 12	12 56	8 92	11 95	6 40	10 51	4 76	8 67	12 15	20 45
63.205	1.33333	6.0	0 00	0 00	1 88	4 23	10 09	6 64	14 89	8 68	13 46	10 18	11 28	10 91	9 61	10 89	9 26	10 21	6 94	9 07	22 58	29.19
63.655	1.30769	6.5	0 00	0 00	1 81	3 62	8.71	5 57	13 07	7 28	12 32	8 63	11 70	9 45	11 12	9 75	9 11	9 52	6 32	8 88	25.84	37.30
64.389	1 26667	7.5	0 00	0 00	1 24	2 69	6 38	4 08	9 44	5 37	9 09	6 43	10 74	7 24	9 91	7 76	8 53	7 96	7 74	7 89	36.92	50.58
65.204	1 22222	9.0	0.00	0.00	0 95	1 89	4 35	2 81	7 63	3.64	6 52	4 44	9 74	5 08	8 00	5 60	7 49	5 97	6 13	6 18	49.19	64 39

* A is the experimental value.

† B is the theoretical value.

relatively good. If a flexible chain were assumed, by using the distribution function of equation 12-42, the distribution would exhibit a maximum value at the pyrophosphate and would not die off quickly enough, so that there would be a small but appreciable quantity of, say, decapolyphosphate. Obviously, the model of a flexible chain does not fit at all in this case, whereas the rigid-rod model corresponds quite well to experiment.

In Figure 12-10, the chromatographic data are compared with the theoretical distribution function, again calculated on the basis of a rigid-rod

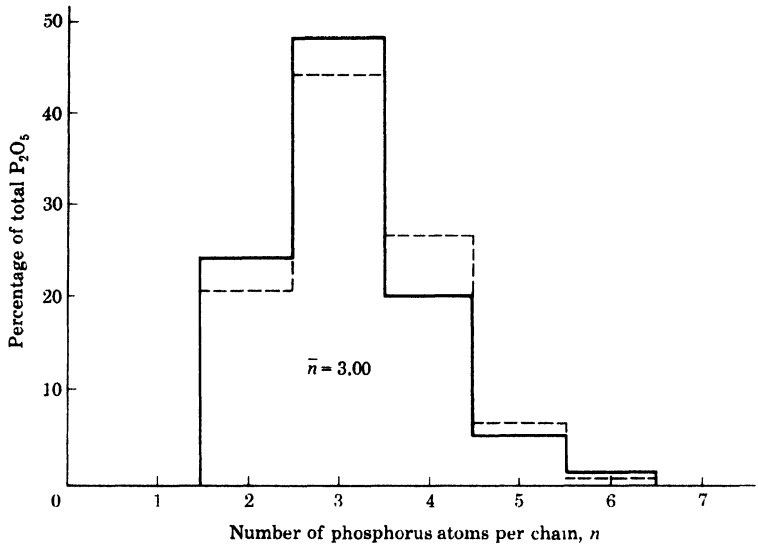


Fig. 12-9. Size distribution of chain phosphates in a sodium phosphate glass for which $R = 1.67$, corresponding to 57.88% P_2O_5. —— Experimental data (paper chromatography). - - - - Calculated from the rigid-rod theory.

model. In this figure it is again seen that experiment and theory agree reasonably well. If the flexible-chain model were chosen, the agreement between experiment and theory would not be nearly so good as for the rigid-rod model, since the distribution function for the flexible chain would turn out to be quite flat and lower than the distribution function for the rigid rod. A bit of flexibility added to the rigid-rod model should give improved agreement between theory and experiment, since this would cause the maximum to move from the value of $n = 8$ to lower values such as the $n = 6$ found for the experimental distribution. However, adding some flexibility to the chain would also tend to give a broader distribution and hence a

somewhat lower maximum than the value of 8% of the total P_2O_5 shown for $n = 8$ in Figure 12-10. The experimental maximum at $n = 6$ corresponds to 10.7% of the total P_2O_5.

In Figures 12-11 and 12-12, the results from solubility fractionation[82] experiments are compared with the two extreme models, the infinitely rigid rod and the infinitely flexible chain. In these figures, the distribution curves are presented on a cumulative basis, since experimental inaccuracies make it impossible to depict the results from fractionation experiments on a stepwise distribution curve such as was used in Figures 12-9 and 12-10.

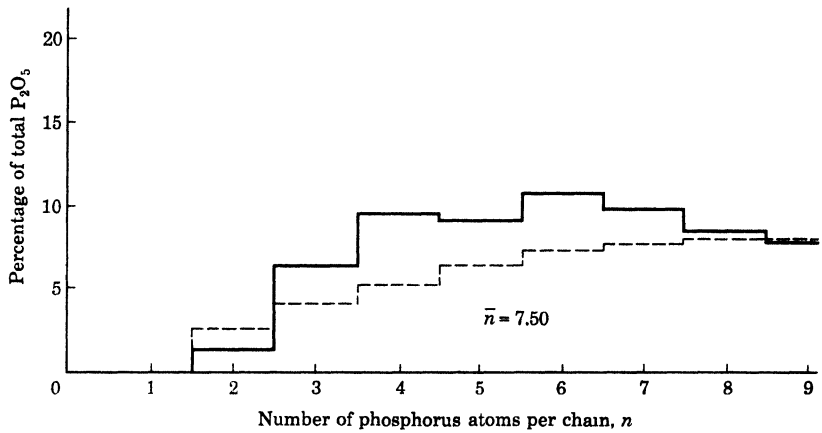


Fig. 12-10. Size distribution of chain phosphates in a sodium phosphate glass for which $R = 1.27$, corresponding to 64.37% P_2O_5. ——— Experimental data (paper chromatography). - - - - Calculated from the rigid-rod theory.

For the glass for which $\bar{n} = 4.6$, the best approximation is given by the rigid-rod model—although the fact that the fractionation procedure does not sharply separate the fractions makes it difficult to compare theory with experiment in this size range. It should be noted that the inability of the solubility fractionation procedure to separate cleanly low members of a homologous series causes the high molecular weight fractions to be abnormally low and the low molecular weight fractions to be abnormally high. In the case of the glass for which $\bar{n} = 16.3$, the experimental data seem to lie about halfway between the theoretical curves corresponding to extreme rigidity and extreme flexibility. This also appears to be the case for the glass for which $\bar{n} = 193$. Obviously, the distributed negative charge along the polyphosphate chain which causes small chains to act as if they were

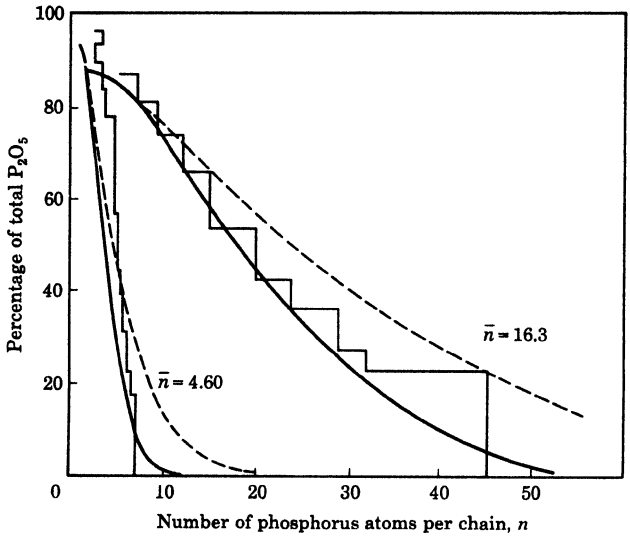


Fig. 12-11. Cumulative size distribution of chain phosphates in two sodium phosphate glasses. Solubility fractionation data are compared with the theoretical distribution functions (smooth curves). ——— Flexible-chain theory. - - - - Rigid-rod theory.

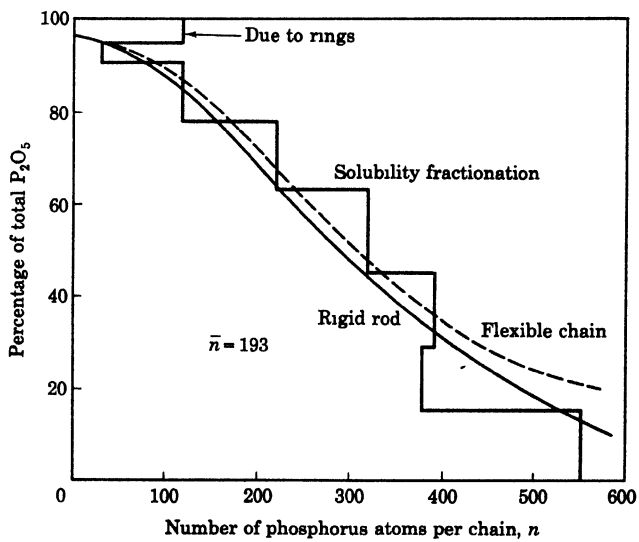


Fig. 12-12. Cumulative size distribution of chain phosphates in a sodium phosphate glass at the metaphosphate composition—a Graham's salt.

rigid rods will not prevent long chains from assuming bowed and gently curved configurations—as long as any segment containing, say, 5–10 phosphorus atoms is essentially straight.

Superimposed upon the distribution of chains described above are the possibilities of (a) crosslinking through branching units, (b) orthophosphate formation, and (c) ring formation—all of which were ruled out in the first-approximation structure theory presented in the previous section of this chapter. A very elegant study of crosslinking has been carried out by Strauss *et al.*,[47] who showed that for the very long chain glasses, having number-average chain lengths in the range of several hundred, approxi-

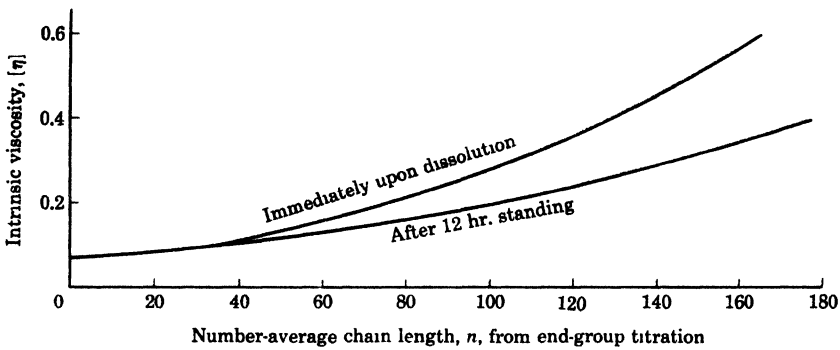


Fig. 12-13. Hydrolysis at branching points are denoted by the intrinsic viscosity. At $\bar{n}$ = about 50, there are no detectable branches. At $\bar{n}$ = 200, there is about 0.1% of the total phosphorus in branching units

mately one out of every thousand phosphorus atoms is a branching unit. Although this amount of crosslinking is so small that it cannot be picked up by usual analytical techniques, it has a pronounced effect on the viscosity number. As predicted theoretically, this crosslinking is very unstable, disappearing completely within about 12 hr. after the sample is dissolved. The rate of degradation at the branching units ranges from 10^3 to 10^5 times greater than the degradation at other parts of the chain under equivalent conditions of pH and temperature. As shown by Figure 12-13, the crosslinking completely disappears[48] when the number-average chain length of the glass is lowered to about 50 since, at that value and below, the intrinsic

[47] U. P. Strauss and T. R. Treitler, *J. Am. Chem. Soc.*, **77**, 1473 (1955); also see U. P. Strauss, E. W. Smith, and P. L. Wineman, *ibid.*, **75**, 3935 (1953).

[48] J. F. McCullough, J. R. Van Wazer, and E. J. Griffith, *J. Am. Chem. Soc.*, **78**, 4528 (1956).

viscosity does not decrease rapidly with time due to scission of crosslinks. Apparently, the presence of crosslinks represents a gradual transition from the polyphosphate region of composition, where first-approximation theory indicates there should be no branching units, to the ultraphosphate region, where branching units must exist. It can be considered that the formation of branching points is a mechanism for avoiding infinitely long chains by the action of equation 12-1.

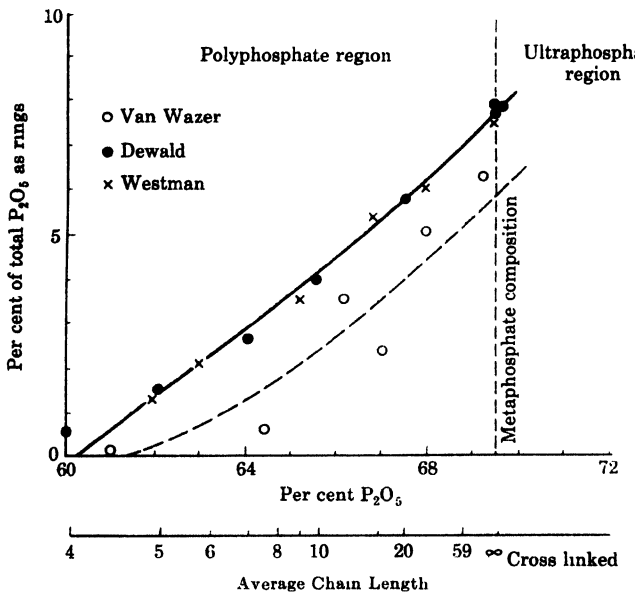


Fig. 12-14. Ring phosphate contained in sodium phosphate glasses as a function of P_2O_5 content of the glasses. The solid circles refer to analyses by barium precipitation, whereas the open circles refer to solubility fractionations with acetone. The crosses refer to paper chromatographic results in which the sum of trimeta- and tetrametaphosphates was measured. There is a constant ratio of about 8 parts of trimeta- to 5 parts of tetrametaphosphate by chromatographic analysis

All reported analyses for orthophosphate content of clean, freshly prepared samples of sodium phosphate glasses for which $1.0 \leq R < 1.7$ indicate that an insufficient amount is present to be detected by the various analytical techniques employed. These techniques are (a) extraction of the yellow phosphomolybdic complex with ethyl acetate, (b) release of the third hydrogen of orthophosphate by silver precipitation, and (c) paper chromatography. It surely appears that there is less than about 0.1% of

the total P_2O_5 present as orthophosphate in those sodium phosphate glasses for which $1.0 \leq Na_2O/P_2O_5 < 1.7$

It should be noted that in both Figures 12-11 and 12-12 the cumulative distribution curves do not go up to 100% of the total P_2O_5. As previously mentioned, this is attributable to the presence of rings in the sodium phosphate glasses. In Figure 12-14 the total P_2O_5 in the form of rings, as determined by barium precipitation,[49] solubility fractionation,[32] and by paper chromatography[26,46] is shown as a function of the P_2O_5 content in sodium phosphate glasses. It appears from this figure that the amount of rings—at least the amount of trimetaphosphate plus tetrametaphosphate—goes from essentially nothing for a glass of the tetrapolyphosphate composition up to a value of about 7.5% of the total P_2O_5 in a glass corresponding to an infinite polyphosphate chain (the metaphosphate composition). It should be noted that the barium precipitation technique agrees very well with the paper chromatographic procedure, and that there is also amazingly good agreement between these two techniques and the relatively crude solubility fractionation procedure. As has been discussed in more detail on page 702, the glasses near the metaphosphate composition (Graham's salt) appear to have a continuous distribution of ring phosphates ranging from the six-membered ring of alternate phosphorus and oxygen atoms (trimetaphosphate) up to rings having as many as, say, fifteen phosphorus atoms in them (ecosimetaphosphate).[48,50] Thus, in a freshly dissolved sample of Graham's salt for which the number-average number of phosphorus atoms in the average chain is 100–125, there is about 4.0% of the total P_2O_5 as trimetaphosphate, 2.5% as tetrametaphosphate, 0.8% as pentametaphosphate, about 0.5% as hexametaphosphate, and apparently lesser amounts of each of the larger rings. Since there seems to be a steady diminution in the amount of each increasingly larger ring phosphate, there should only be a small fraction of a per cent of the total P_2O_5 found as the ecosimetaphosphate. Comparison of the data in Figure 12-14 with the chromatographic results on rings larger than the tetrametaphosphate indicates that rings containing more than four or five phosphorus atoms probably cannot be distinguished from chains by either the barium precipitation procedure or the solubility fractionation technique

Effect of Changing Cations

In a very recent study,[29] Westman and Gartaganis have carried out chromatographic separations on lithium, sodium, and potassium phosphate

[49] W. Dewald and H. Schmidt, *Z. anorg. u. allgem. Chem.*, **272**, 253 (1953).

[50] J. R. Van Wazer and E. Karl-Kroupa, *J. Am. Chem. Soc.*, **78**, 1772 (1956).

glasses. In Figure 12-15, the size distributions for lithium, sodium, and potassium phosphate glasses having an average chain length of three are compared with the rigid-rod and flexible-chain distribution functions. The glass based on lithium is seen to exhibit a distribution curve part way between that expected for the ideal rigid rod and that for a flexible chain. As previously noted, the sodium glass approximates the rigid-rod model. However, the potassium glass distribution lies close to that of the flexible-chain model

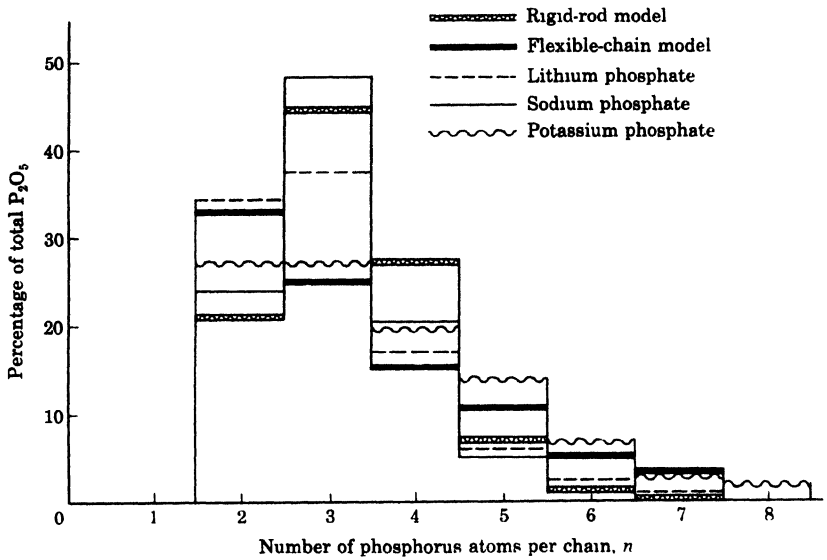


Fig. 12-15. Size distribution of chain phosphates in various phosphate glasses for which $\bar{n} = 3.0$.

In Figure 12-16, size-distribution plots are given for lithium, sodium, and potassium phosphate glasses exhibiting an average chain length of seven. In all cases, the experimentally observed distributions are sharper and peak at somewhat lower chain lengths than do the distribution curves for either the rigid-rod or flexible-chain models. It is believed that the error is due to omitting (1) the finite packing volumes of the polyphosphate chains and (2) the polarizability of the charges. Both of these oversimplifications should cause maximum error at intermediate chain lengths—with the very short and the very long chains giving a better fit. The data in Figures 12-15 and 12-16 indicate that the lithium ions may be somewhat associated with the

chain anions, perhaps by fitting between oxygen atoms (two per PO_4 group) not in the P—O—P chain, and that the potassium ions may be polarized to an appreciable extent. It is obvious that additional physical measurements, other than size-distribution determinations, are needed to interpret fully the differences observed between the distribution curves of the glassy phosphates based on lithium, sodium, and potassium.

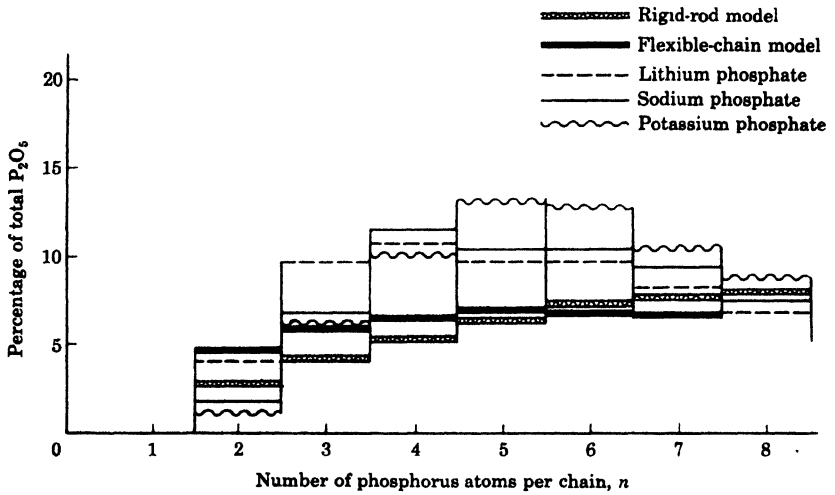


Fig. 12-16. Size distribution of chain phosphates in various phosphate glasses for which $n = 7.0$.

Amorphous Sodium Acid Phosphates

A series of amorphous sodium acid phosphates containing equimolar amounts of Na_2O and H_2O but varying proportions of these to P_2O_5 has been studied recently at the Ontario Research Foundation.[28] Since the data obtained by these investigators were somewhat erratic and appeared to be subject to appreciable experimental error, the values were smoothed graphically, normalized, resmoothed, and then again normalized so that the sum of the number of moles of Na_2O corresponding to the various species of molecule-ions divided by the sum of the P_2O_5 in these same molecule-ions equaled the observed value of R. The equilibrium constants K_3 and K_3' were then calculated and found to vary, as shown in Figure 12-17. From this plot, K_3 rather than K_3' was chosen to use in calculating the theoretical curves shown in Figure 12-18. It should be noted that the treatment of the data employed in Figures 12-17 and 12-18 assumes an average cation

TABLE 12-3

Molecular Composition of Sodium Acid Phosphate Glasses (Na_2O–H_2O) Compared with the Theoretical Composition Calculated from the Flexible-Chain Model

Item no.	Analysis: Wt.-% P_2O_5	Analysis: (Na_2O + H_2O)/P_2O_5 R	Analysis: Overall $\bar{n}$	n Corrected for unreacted H_2O	Percentage of total P_2O_5 as: Ortho A*	Ortho Bt	Pyro A	Pyro B	Tripoly A	Tripoly B	Tetrapoly A	Tetrapoly B
1	55 0	2 93	1 05	1 45	40 3	--	51 7	52 2	7 96	6 66		0 76
2	56 0	2 79	1 12	1 54	34 4	- -	52 5	52 9	11 5	10 4	1 61	1 83
3	57 0	2 68	1 19	1.63	29 4	-	52 0	52 4	14 8	14 0	3 09	3 30
4	58 0	2 57	1 27	1 72	25 6	-	50 2	50 6	17 8	16 9	4 66	5 01
5	59 0	2 47	1 36	1 81	22 7	-	47 0	47 4	20 5	19 3	6 16	7 02
6	60 0	2 37	1 46	1 89	20 8	- -	43 7	44 3	22 3	20 8	7 60	8 69
7	61 0	2 27	1 58	1 96	19 1	-	40 6	41 3	23 5	21 8	9 18	10 2
8	62 0	2 18	1 70	2 05	17 7	-	37 4	38 2	24 1	22 3	10 6	11 5
9	63 0	2 08	1 84	2 14	16 2	-	34 13	35 0	24 1	22 4	12 1	12 7
10	64 0	2 00	2 01	2 21	14 9	-	31 0	31 9	23 6	22 2	13 3	13 7
11	65 0	1 91	2 19	2 39	13 3	—	27 5	28 0	22 5	21 4	14 1	14 5
12	66 0	1 83	2 41	2 57	11 6	—	24 2	24 5	21 1	20 3	14 6	14 9
13	67 0	1 75	2 67	2 75	10 3	—	21 7	21 6	19 4	19 0	14 8	14 9
14	68 0	1 67	2 98	-	8 97	- -	19 1	18 1	17 7	17 1	14 3	14 4
15	69 0	1 63	3 18		7 66	—	16 8	16 5	15 9	16 2	14 3	14 1
16	70 0	1 57	3 51	—	6 52	—	14 4	13 8	14 1	14 3	13 3	13 1
17	71 0	1 51	3 92	--	5 25	—	11 9	10 9	12 3	11 9	12 0	11 6
18	72 0	1 44	4 54	—	3 94	—	9 25	8 27	10 1	9 55	10 4	9 80

* A is the experimental value.

† B is the theoretical value.

which partakes of the properties of both the sodium and hydrogen. The values of K_1 and K_2 indicate that this hypothetical average cation is quite strongly associated with the phosphate anions. Indeed, this hypothetical ion is seen to act much like the hydrogen ion and is very different from the sodium ion with respect to the building-unit equilibrium constants.

In Table 12-3 the smoothed experimental data concerning the distribution of molecule-ions in various sodium acid phosphate glasses are compared with the predictions derived from the assumption of a flexible chain (see equation 12-44). It should be noted that the agreement is quite good. This is graphically illustrated by Figures 12-19 and 12-20, which show that the flexible-chain model is a good approximation to the state of affairs existing in vitreous sodium acid phosphates in which there are equimolar amounts of Na_2O and P_2O_5. On the average, the sodiums and hydrogens should alternate along a given phosphate chain; and thus, it appears that merely separating a pair of negative charges (counterbalanced by a pair of sodium ions) by an associated hydrogen lends sufficient flexibility to a phosphate chain so that the infinitely flexible model represents a reasonable approxi-

TABLE 12-3 (*continued*)

Item no	Percentage of total P_2O_5 as (*continued*)											
	Pentapoly		Hexapoly		Heptapoly		Octapoly		Nonapoly		Higher	
	A	B	A	B	A	B	A	B	A	B	A	B
1												
2												
3	0.699	0 730		0 140								
4	1 79	1 39		0 370								
5	2 78	2 39	0 894	0 780								
6	3 80	3 40	1 80	1 28	-	0 47						
7	4 94	4 47	2 72	1 88								
8	5 99	5 61	3 65	2 62	0 711	1 19						
9	7 05	6 79	4 60	3 47	1 74	1 73		0 84				
10	7 97	7 94	5 52	4 41	2 76	2 39	0 920	1 26		0 66		
11	8 84	9 25	6 33	5 65	3 61	3 36	1 81	1 95	0 904	1 12	1 20	1 44
12	9 55	10 3	6 99	6 82	4 63	4 40	2 66	2 78	1 77	1 72	2 86	2 67
13	10 2	11 0	7 62	7 74	5 37	5 31	3 42	3 52	2 44	2 36	4 78	4 27
14	10 7	11 4	8 38	8 62	6 04	6 34	4 19	4 58	3 12	3 25	7 02	7 20
15	11 1	11 5	9 03	9 00	6 68	6 86	4 91	5 12	3 63	3 76	9 92	9 34
16	11 2	11 3	9 18	9 32	7 31	7 49	5 53	5 90	4 05	4 57	14 1	13 7
17	10 7	10 8	9 61	9 26	7 73	7 89	5 85	6 59	4 26	5 41	20 5	20 7
18	9 64	9 13	9 25	8 72	7 97	8 28	5 90	7 29	4 23	6 31	28 9	28 4

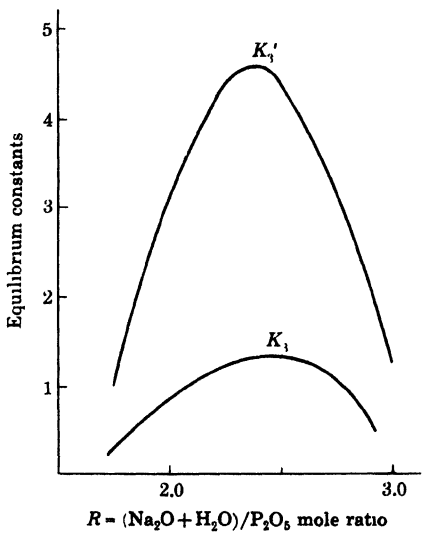


Fig 12-17 Variation of the equilibrium constants for formation of unreacted water in the sodium acid phosphate glasses for which $Na_2O = H_2O$.

mation to the true state of affairs. The equilibria between the various phosphate building units and orthophosphate also seem to be very sensitive to a relatively small amount of association, since Figure 12-18 indicates that a mixture of half sodium and half hydrogen acts very similarly to the condensed phosphoric acids in which there is no sodium. Presumably, the study of amorphous compositions in which the Na_2O/H_2O mole ratio

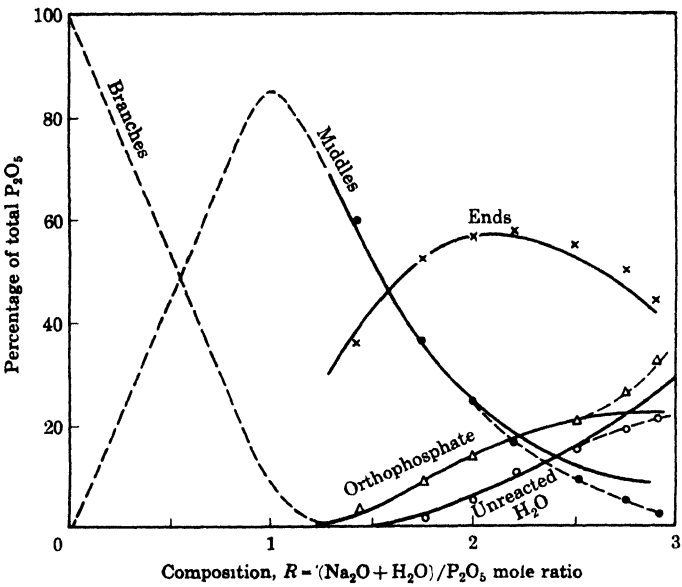


Fig. 12-18. Relative proportions of branching, middle, and end units as well as orthophosphate and free water as a function of the $(Na_2O + H_2O)/P_2O_5$ mole ratio for $Na_2O = H_2O$. The smooth curves are calculated on the assumption that $K_1 = 0.01$, $K_2 = 0.10$, and $K_3 = 1.00$.

was varied from zero to infinity would lead to an approximate numerical relationship between the values of the various K's (building-unit equilibrium constants) and the amount of association of the cations with the chain phosphate molecule-ions. Such an experiment would also offer a semiquantitative approach to study of the Antibranching Rule. Of course, a mixture of organic radicals (methyl groups) and quaternary ammonium ions (tetramethylammonium ion) would be more amenable to a direct theoretical interpretation than the sodium-hydrogen mixture discussed here. However, there may be a problem of achieving equilibrium in such a system.

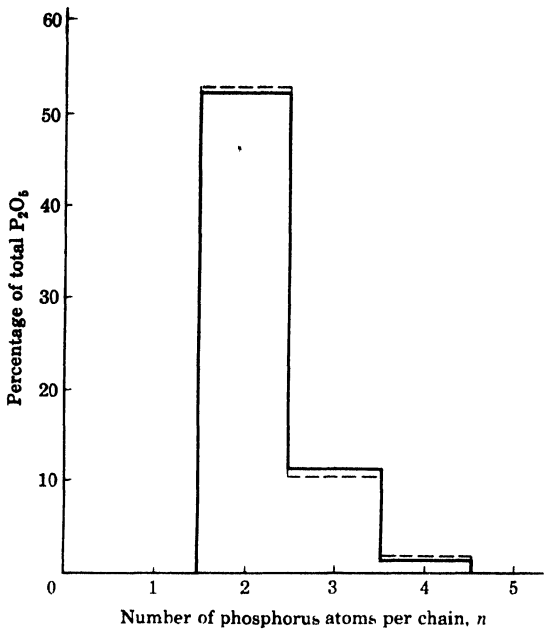


Fig 12-19 Size distribution of chain phosphates in a sodium acid phosphate glass for which R = 2 79, corresponding to 56.0% P_2O_5. – – Experimental data (paper chromatography). - - Calculated from the flexible-chain theory.

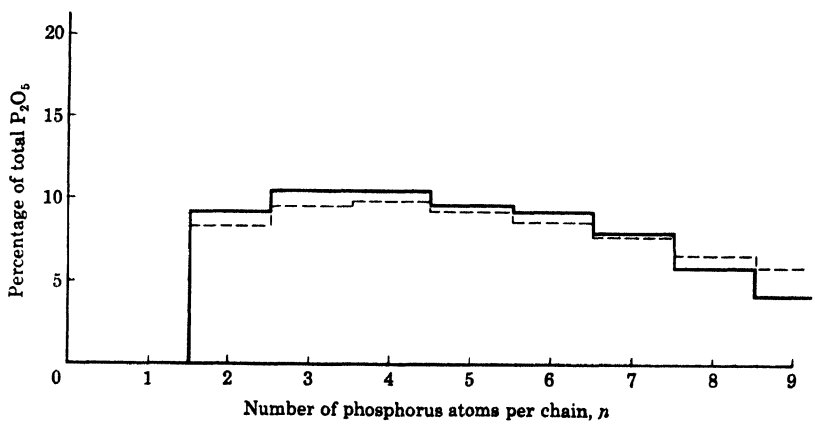


Fig. 12-20. Size distribution of chain phosphates in a sodium acid phosphate glass for which R = 1.44, corresponding to 72.0% P_2O_5. ——— Experimental data (paper chromatography). – – – – Calculated from the flexible-chain theory.

PHYSICAL AND CHEMICAL PROPERTIES

Preparation and Properties of Condensed Phosphoric Acids

In the H_2O–P_2O_5 system there is a complete series of amorphous compositions ranging from pure water to pure vitreous phosphorus pentoxide. Indeed, in this system only a few crystalline compositions are known. These are the hemihydrate of orthophosphoric acid ($4\ H_2O \cdot P_2O_5$), orthophosphoric acid itself ($3\ H_2O \cdot P_2O_5$), and pyrophosphoric acid ($2\ H_2O \cdot P_2O_5$). In addition, crystalline tetraphosphoric acid[51] ($3\ H_2O \cdot 2\ P_2O_5$) and crystalline metaphosphoric acid[52] ($H_2O\ P_2O_5$(?) or perhaps an ultraphosphate) have also been described in the literature. It is now rather generally known that the reported crystalline "tetraphosphoric acid" was really crystalline pyrophosphoric acid which slowly crystallizes from condensed phosphoric acids in the approximate range between the H_2O/P_2O_5 mole ratios of 1.4 and 2.3. Although repeated attempts in the Monsanto laboratories to make the soluble crystalline metaphosphoric acid described by Rechid have failed, it is still possible that such a material really exists, since Mme. Rechid found an x-ray pattern for it.

The amorphous condensed phosphoric acids range from syrupy liquids to glasses which have a sufficiently low viscosity (about 10^8–10^9 poises at 25°C.) to flow slowly at room temperature. Although the condensed phosphoric acids of high viscosity shatter when struck with a hammer, they also will flow into the shape of their container when stored for several days. All of the condensed phosphoric acids are colorless when pure. An interesting phenomenon is observed in the phosphoric acids near the azeotropic composition ($R = H_2O/P_2O_5 = 0.7$) where the glassy acids decrepitate during dissolution in water. When in contact with water, these acids emit a crackling noise and numerous small particles are violently ejected from their surface. Obviously, the interaction of water with such ultraphosphoric acids causes density changes which lead to fracture near the surface. This odd behavior can be attributed to rapid hydrolysis of the top layers of branching points which are held into the structure by branching points not yet exposed to the action of the water.

Neither the ortho- nor pyrophosphoric acids crystallize readily. In fact, solidification of liquid pyrophosphoric acid, $H_4P_2O_7$, due to crystallization takes several months at room temperature. This slow rate of crystallization may be due to the reorganization process but more probably is dif-

[51] M. A. Rakuzin and A. A. Arseniev, *Chem. Z.*, **47**, 195 (1923); *Zhur. Fiz. Khim.*, **53**, 376 (1921).

[52] Mme. Réchid, *Compt. rend.*, **196**, 860 (1933).

fusion controlled The viscosities of the condensed phosphoric acids given in Figure 12-21 are approximate, since accurate data are not available except for the orthophosphate and azeotrope[53] compositions. The densities of the condensed phosphoric acids are, to a first approximation,[53] proportional to the amount of phosphorus in their composition, according to the following equation:

$$d_{25°C.} = 0.0167\ (\%\ P_2O_5) + 0.66 \qquad \text{for } 50 < P_2O_5 < 95 \quad (12\text{-}67)$$

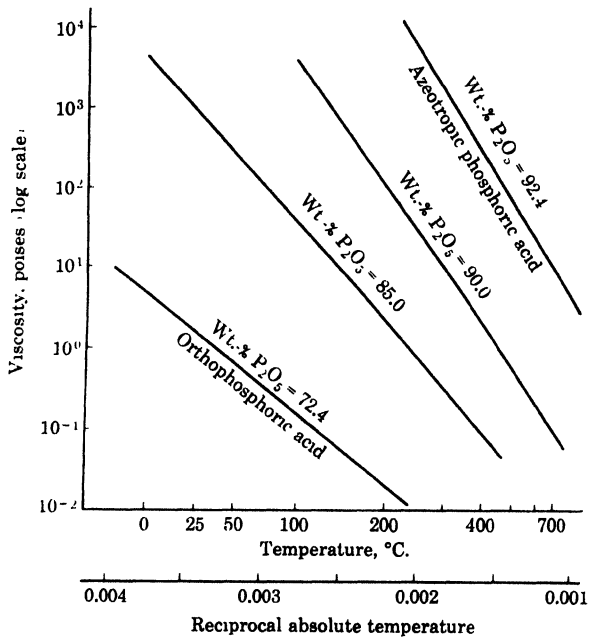


Fig. 12-21. An approximate plot of the viscosities of several condensed phosphoric acids.

As is the usual case, the density of the condensed phosphoric acids decreases with a rise in temperature. The densities given by equation 12-67 can be approximately corrected to other temperatures by subtracting the value $0.0009\ (t - 25°)$, where t is the temperature in °C.

The amorphous condensed phosphoric acids containing less than about 91% P_2O_5 can readily be made by evaporating orthophosphoric acid or by adding phosphorus pentoxide to phosphoric acid. The process of preparing condensed phosphoric acids by boiling the water out of orthophosphoric

[53] E. J. Griffith, unpublished data from the Monsanto Chemical Co.

acid is usually carried out by heating in a gold or platinum crucible. During this heating operation, the acid becomes colored[54]—purple when a gold crucible is used and brown when a platinum crucible is used. The intensity of this coloration depends on the length of time the acid was heated and on the temperature. When the water is boiled off promptly in an electric furnace to give an acid containing 89% P_2O_5 or less, the coloration is hardly noticeable—especially if a gold crucible is used, since the gold is somewhat less readily attacked by hot phosphoric acids than is the platinum. However, by continued heating or by repeatedly adding and boiling out water, the coloration due to gold or platinum in the condensed phosphoric acids can be made quite intense—a deep reddish amber in the case of the platinum. The color due to either gold or platinum is very stable, remaining unchanged when the acid was stored for several years at room temperature.[54]

Condensed phosphoric acids made by adding phosphorus pentoxide to orthophosphoric acid are apt to be somewhat dark-colored (greyish), probably because of the presence of traces of the lower oxides of phosphorus. This coloration, however, can be readily removed by mixing a few drops of nitric acid into the hot mixture. When phosphorus pentoxide is added to the more condensed phosphoric acids, it is usually necessary to heat the mixture in order to effect dissolution. Acids containing more than about 91% P_2O_5 (the azeotropic composition) must be made by combining either water or a phosphoric acid with phosphorus pentoxide. Such acids have received very little study.

When aerated, the condensed phosphoric acids are quite corrosive to a large number of metals, but the rate of attack of these acids on metal is considerably reduced when the metal surface is protected from air.[40] However, at temperatures above several hundred °C., the acids are all extremely corrosive both to metals and ceramic materials. The best containers for high temperatures are gold and platinum. Graphite is satisfactory when the temperature is no greater than about 350°C., at which point the rate of reduction of the phosphoric acid to elemental phosphorus becomes appreciable.

The condensed phosphoric acids serve as useful reagents in organic chemistry,[55] where they aid in ring closures and in rearrangements. The long

[54] A. Müller, F. Urbach, and F. Blank, *Kolloid-Z.*, **44**, 185 (1928); also see G. E. Rindone and J. L. Rhodes, *J. Am. Ceramic Soc.*, **39**, 173 (1956) for information about platinum in sodium phosphate glasses.

[55] F. D. Popp, review (to be published); Anon., *Chem. Eng. News*, **30**, 4130 (1952). K. C. Kennard, *D.P.I. Org. Chem. Bull. (Eastman Kodak Co.)*, **29**, No. 1, 1 (1957).

chain phosphoric acids, commonly known as "metaphosphoric acid," are employed as reagents in the precipitation of proteins. Because the viscosity of the pure acids is not sufficiently great so as to keep the individual particles from coalescing and flowing so as to fill the container like a liquid, commercial preparations of so-called "metaphosphoric acid" contain Na_2O in addition to the normal H_2O and P_2O_5. The most recent review of reagent chemicals[56] by the American Chemical Society says that "metaphosphoric acid," otherwise known as vitreous sodium acid metaphosphate, contains as a "preservative" a somewhat greater proportion of sodium metaphosphate than that corresponding to the empirical formula, $NaH(PO_3)_2$.

Vaporization of Condensed Phosphoric Acids

The boiling points of the various acids in the H_2O–P_2O_5 system are shown in Figure 12-22, where it should be noted that there is little change in the boiling point until the composition corresponding to about 65% P_2O_5 is reached, after which the boiling temperature increases rapidly. The condensed phosphoric acids exhibit an azeotrope in the ultraphosphate composition range.[57] At a pressure of 760 mm. of Hg, the azeotrope comes at a composition of about 92.4% ($R = 0.65$) and has a boiling point of 864°C. At lower pressures, the composition of the azeotrope moves toward the H_2O end of the diagram. Thus, at 104 mm. of Hg, the composition of the azeotrope corresponds to 91.1% P_2O_5 ($R = 0.77$).

The vapor pressures of the condensed phosphoric acids have been measured over a considerable range of temperature and composition.[58] The vapor pressure data have been systemized into the following equation, which fits the data within experimental error in the range from 50–100 mm. to 760 mm. of Hg over the composition range of 20–92% P_2O_5.

$$\log p_{\text{mm.}} = 8.7788 - (5.9080 \times \text{b.p.}/T) \qquad (12\text{-}68)$$

where $p_{\text{mm.}}$ is the vapor pressure in millimeters of Hg of the given acid at a temperature of T in °K., and b.p. is the boiling point of the acid in °K. as measured at 760 mm. of Hg. The values of b.p. as a function of composition can be obtained from Figure 12-22.

The approximate composition of the vapor of phosphoric acids of vari-

[56] E. Wichers *et al.*, *Reagent Chemicals*, American Chemical Society, Washington, D. C., 1955, pp. 266–67.

[57] G. Tarbutton and M. E. Demming, *J. Am. Chem. Soc.*, **72**, 2086 (1950). For a typical early misinterpretation of azeotrope data, see D. Balareff, *Z. anorg. u. allgem. Chem.*, **102**, 34 (1917).

[58] E. H. Brown and C. D. Whitt, *Ind. Eng. Chem.*, **44**, 615 (1952).

ous composition boiling at 760 mm. pressure is also given in Figure 12-22 It can be seen from this curve that acids containing up to about 75% P_2O give off very nearly pure water when boiled and that, in the range from 75 t 85% P_2O_5 in the boiling liquid, the vapor changes from mildly acidic wate to a highly concentrated acid, having a concentration near that of the azeo trope.

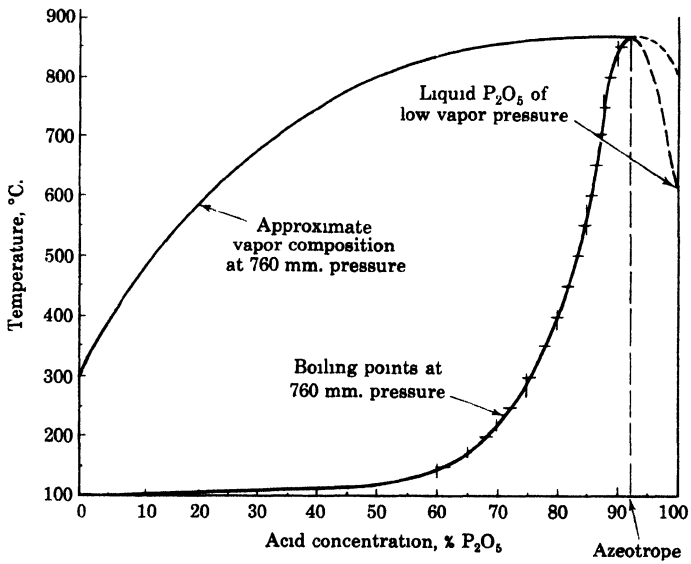


Fig. 12-22 Temperature composition diagram for the system H_2O-P_2O_5.

The apparent molecular weights[58,59] of the vapors obtained at 1020°C. by volatilizing phosphoric acids having several different values of the H_2O/P_2O_5 mole ratio are reported in Table 12-4. According to these values, vaporized phosphoric acids consist of a mixture of water plus P_4O_{10} vapor and/or a low molecular weight ultraphosphate, such as HP_3O_8. The molecular weights calculated for these two compounds are compared with average values of the measured molecular weights in Table 12-4. Probably the vapor consists of water plus several low molecular weight ultraphosphoric acids, including the low molecular weight ultimate ultraphosphate, P_4O_{10}.

[59] W. A. Tilden and R. E. Barnett, *Trans. Chem. Soc. (London)*, **69**, 154 (1896)

TABLE 12-4
Apparent Molecular Weights of Vapor in the H_2O–P_2O_5 System at 1020°C

Mole ratio H_2O/P_2O_5	Per cent P_2O_5	Acid composition	Measured molecular weights	Average value	Calc. mol. wt. assuming vapor is $H_2O + P_4O_{10}$	Calc mol. wt assuming vapor is $H_2O + HPO_3$
4 84	61 5	85% H_3PO_4	43 8 44 7 45 8 44 8	44 8	42 4	43 7
3 00	72 4	Pure H_3PO_4	58 7 50 0 59 2	56 0	56 0	58 8
1 08	88 0	Near "metaphosphoric acid"	108 7 108 4 111 8	109 6	102 4	107 8
0 86	90 2	Near azeotropic acid	143 (corrected = 122); 138 (corrected = 117)	120[a]	115 8	127 2
0 79	90 9	Near azeotropic acid	140 (corrected = 119); 139 (corrected = 118)	118[a]	121 0	138 7
0 69	92 0	Azeotropic acid	132 0 123 5 135 5 137 0 133.0 130.2 134 0	132 2	130 0	153 0

[a] Value from ref 59, all other values from ref 57

Vitreous Sodium Phosphates

From pure phosphorus pentoxide, P_2O_5, all the way to the pyrophosphate composition, $2\ Na_2O{\cdot}P_2O_5$, there is a continuous series of vitreous sodium phosphates. Within this series, the range between pure P_2O_5 and the metaphosphate composition, $Na_2O{\cdot}P_2O_5$, is little known; and glasses in the range from the tripolyphosphate composition, $5\ Na_2O{\cdot}3\ P_2O_5$, to the pyrophosphate composition have been prepared only recently.[46] Although the first known glassy sodium phosphates were discovered in 1833,[2] and many other glasses between the metaphosphate and tripolyphosphate compositions were made before the middle of the 19th century, it was not until the

end[60] of that century that their amorphous glassy character was fully realized by a few authors; and indeed until a few years ago, many reputable scientists said that these glasses were mixtures of fine crystallites or a mixture of the glass for which $Na_2O/P_2O_5 = 1$ with pyrophosphate (presumably crystalline).

The glass of the metaphosphate composition usually obtained by melting monosodium orthophosphate has been called Graham's salt in much of the scientific literature. It is also known as "sodium hexametaphosphate" because of the misinterpretation of some early chemical and physical measurements[61] which today receive an entirely different, more sophisticated interpretation. The term "hexametaphosphate" has also been broadly extended to cover the range of vitreous sodium phosphates between the meta and pyro compositions. In addition, the term has often been used to describe a glass* having an Na_2O/P_2O_5 mole ratio of about 1.1 instead of the metaphosphate mole ratio of 1.00. In some of the technological literature of the last 25 years, the terms "hexametaphosphate," "tetraphosphate," and "septaphosphate" have loosely been employed as names for practically any of the glasses between the tripolyphosphate and the metaphosphate compositions. However, the majority of authors have used these terms properly to describe the glasses, the average composition of which corresponds to the names; but this cannot be depended upon. Thus, essentially anhydrous glasses for which the Na_2O/P_2O_5 mole ratio $= (\bar{n} + 2)/\bar{n} = 1.50$ and 1.285 should be called tetrapoly- and septapolyphosphate compositions, respectively.

In view of the fact that a ring metaphosphate containing six phosphorus atoms has now been described,[50] it is very undesirable to continue the misnomer "hexametaphosphate" as a name for vitreous sodium phosphates near the metaphosphate composition. The proper way of naming phosphate glasses is to describe them in terms of either (1) the Na_2O/P_2O_5 mole

[60] For example, T. Salzer, *Arch. Pharm.*, **232**, 371 (1894).

[61] T. Fleitmann, *Ann. physik.*, **78**, 233, 338 (1849) tentatively assigned the vitreous sodium metaphosphate, $(NaPO_3)_x$, a degree of polymerization of six because of the composition of some "double salts" which were undoubtedly amorphous. He reasoned on the basis of combining weights that the "valence" of the phosphate radical must be six. Later studies by Pascal and coworkers [*e.g.*, P. Pascal and Mme. Réchid, *Compt. rend.*, **194**, 761 (1932); P. Pascal, *ibid.*, **177**, 1298 (1923)] also showed a six-fold degree of polymerization of the "hexametaphosphate" from electrical conductivity interpreted according to the obsolete Ostwald-Walden Rule. It is not clear from the work of Pascal whether the "hexametaphosphate" he described is really equivalent to Graham's salt.

* The trade name Calgon for a 1.1 $Na_2O \cdot P_2O_5$ glass has also been used to a considerable extent in the technical literature.

ratio, (2) the number-average or other specified average chain length, or (3) the average composition as in the phrase "sodium phosphate glass corresponding to the tetrapolyphosphate composition." Naming sodium phosphate glasses according to their Na_2O/P_2O_5 mole ratio applies to all glasses, both in the ultraphosphate and polyphosphate composition ranges. However, names based on chain lengths or average compositions in terms of polyphosphates can only be applied to the glasses for which the Na_2O/P_2O_5 mole ratio is equal to or greater than unity.

Preparation of Vitreous Sodium Phosphates

The preparation of vitreous sodium phosphates between the metaphosphate ($Na_2O \cdot P_2O_5$) and the tetrapolyphosphate ($1.5\ Na_2O \cdot P_2O_5$) compositions is a relatively simple matter. In the laboratory, the starting ingredients are usually melted in a platinum crucible at temperatures lying above the liquidus of Figure 10-1 (see p. 604) and usually below about 1000°C. The melt is then poured onto a chill plate which can be made of copper or some other good heat-conducting metal and which ought to be water-cooled when a large number of preparations are made consecutively. The glasses having more Na_2O than corresponds to the tetrapolyphosphate composition (about 60.5% P_2O_5) must be chilled very rapidly to prevent crystallization. In order to make a glass exhibiting the tripolyphosphate composition, it is necessary to throw the melt quickly between the chill plates which are then instantly slammed together. In this case, the chill plates should be made of either heavy copper or silver.

The preparation of vitreous phosphates having more Na_2O than corresponds to the tripolyphosphate composition must be carried out by a technique in which the chilling is considerably more rapid than is obtained by normal methods of quenching. Preliminary experiments by Westman *et al.*[46] indicate that sodium phosphate glasses ranging from the tripolyphosphate composition down to the orthophosphate composition ($3\ Na_2O \cdot P_2O_5$) can be made in an apparatus where the charge is injected into a flame.

Since the vitreous sodium phosphates consist of a mixture of Na_2O and P_2O_5, with only trace amounts of other ingredients, any combinations of raw materials which upon heating will leave only Na_2O and P_2O_5 can be used in their preparation. Thus, glasses for which Na_2O/P_2O_5 is greater than about 0.9 can be made from such mixtures as (1) Na_2CO_3 plus H_3PO_4, (2) $NaPO_3$-I plus $Na_4P_2O_7$, (3) Na_2O plus P_2O_5, (4) NaCl plus H_3PO_4, especially when steam is blown through the melt to remove residual chloride as HCl, (5) $Na(NH_4)HPO_4$ plus $NaCO_3$ (if needed), and (6) Na_3PO_4 or Na_2HPO_4 plus $NH_4H_2PO_4$.

As shown by Figure 12-23, the average chain length of the phosphate molecules making up the glass in the polyphosphate composition range ($1 < Na_2O/P_2O_5 < 2$) increases very slowly with increasing P_2O_5 content until, shortly before the metaphosphate composition, at about 66% P_2O_5, the

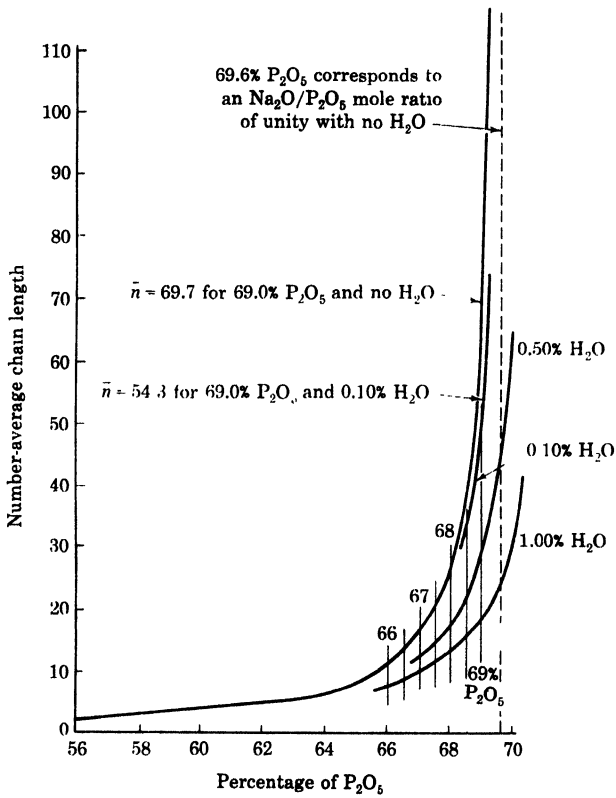


Fig. 12-23. Number-average chain length of sodium phosphate glasses as a function of P_2O_5 and water content, assuming only chains with no rings, ortho, or branching points.

average chain length increases rapidly, approaching infinity at the exact metaphosphate composition of 69.6% P_2O_5. In the region between 66 and 69.6% P_2O_5, the average chain length is very dependent on traces of water and other substances which can play a cationic role in the glass so as to act as chain breakers. Thus, in a system containing only Na_2O, P_2O_5, and

traces of H_2O, the number-average chain length $\bar{n}$ is given by the following equation, which is simply a rearranged version of equation 12-49:

$$(Na_2O + H_2O)/P_2O_5 = (\bar{n} + 2)/\bar{n} \qquad (12\text{-}69)$$

with $Na_2O >> H_2O$. Equation 12-69 is derived from the approximation that only chains are present in the glasses, and this also applied to the curves in Figure 12-23 showing the effect of traces of water of composition.

When glasses in which the Na_2O/P_2O_5 mole ratio is exactly unity are prepared by merely melting monosodium orthophosphate at, say, 700°C., the average chain length usually lies in the range of 20 to 50 because of the residual water of composition. In order to get glasses of higher chain length, it is necessary to heat the melt for a long time. Another technique for removing water from such melts is to cycle the temperature above and below the value at which the melt crystallizes. Under these conditions, each time crystallization takes place, some of the water is released in a burst. The longest number-average chain lengths found in samples of Graham's salt lie in the range of 250 to 500 phosphorus atoms per chain. Such chain lengths have been achieved by either holding the melt for approximately a month at temperatures between 700 and 800°C. or cycling between 700 and 500°C. about a dozen times over a period of many days. Present information indicates that the chain lengths of polyphosphate glasses are not noticeably dependent upon the temperature of the melt or the rapidity of cooling as long as the cooling is fast enough so that no crystallization occurs. In other words, the final material should be amorphous by x-ray diffraction and should show no small crystals under the microscope. These conditions are achieved when the fresh glass is completely clear and transparent. The disadvantage of keeping glasses molten for extended lengths of time is found in their corrosiveness, even to platinum, which will be discussed in more detail below.

Vitreous sodium ultraphosphates for which the Na_2O/P_2O_5 mole ratio is less than about 0.9 exhibit appreciably high partial pressures of P_2O_5, as well as a strong tendency to absorb water while molten, so that they are best prepared in sealed tubes or bombs. Vitreous sodium ultraphosphates have been made in Vycor ampules and in sealed steel bombs, both with and without platinum liners. (It is desirable to separate the platinum liner from the steel by ceramic spacers.)

Corrosiveness of Molten Phosphates

Molten sodium phosphates, as well as other phosphate melts, are extremely good solvents and, indeed, this is the basis of the microcosmic bead

test, which played such an important role in chemistry in the days of blowpipe analysis.[62] Microcosmic salt, $Na(NH_4)HPO_4$, which upon heating gives a sodium metaphosphate glass, was chosen because of its phenomenally good dissolving action on various metal salts and oxides.

When phosphate melts are prepared in platinum, precautions must be taken, since the presence of traces of reducing materials in the molten phosphate will cause the platinum to crack and disintegrate. At melt temperatures, carbon and other reducing substances, such as the silicon carbide often used in furnace linings, cause the formation of elemental phosphorus from molten sodium phosphates. This produces platinum phosphides which preferentially form at grain boundaries in the platinum.[63] In order to protect platinum containers from reducing substances which might be in the furnace, it is usually advisable to set them upon clean, unglazed, ceramic tiles.

In some industrial furnaces in which sodium phosphates are melted, zirconia bricks are used as linings. Such bricks are relatively resistant to corrosion by phosphates. However, crucibles made of this material do not work out very well in the laboratory because the large surface/volume ratio of small equipment leads to an undesirably rapid build-up of dissolved zirconia in the melt. The usual porcelain crucible is also badly attacked by molten phosphates and should not be employed in laboratory preparations in which sodium phosphates are melted. At temperatures above about 400°C., graphite should not be used because of reduction of phosphates to elemental phosphorus. At 700°C., a sodium phosphate melt in a graphite or carbon crucible exhibits tiny spurts of flame at the surface with some phosphorus being lost from the melt. The best container for molten phosphates is a frozen lining of the melt itself.[64] However, this cannot conveniently be used in small installations.

In view of this information, it is recommended that, in order to achieve highest purity, vitreous sodium phosphates for which Na_2O/P_2O_5 is equal or greater than unity be made by simply melting together in the proper ratio well-dehydrated portions of crystalline $NaPO_3$ and $Na_4P_2O_7$. The melting should be carried out promptly by placing the well-mixed ingredients contained in a platinum dish into a preheated furnace. Stirring with a platinum rod before chilling insures homogeneity of the glass. The $Na_4P_2O_7$

[62] W. Elderhorst, *Manual of Blowpipe Analysis*, D. Van Nostrand Co., New York, 1867.

[63] A. Jedele, *Z. Metallkunde*, **27**, 271 (1935); H. J. Frost, *Chem.-Ztg.*, **65**, 14 (1941).

[64] For example, F. P. Kershbaum, U. S. Pat 2,142,943; 2,142,944 (1939, assigned to the Monsanto Chemical Co.)

can be dehydrated in porcelain by heating C. P. $Na_4P_2O_7 \cdot 10\ H_2O$ for several days at about 200°C. or higher, followed by cooling and grinding, and then reheating to about 350°C. in porcelain. The dry crystalline $Na_4P_2O_7$ and $NaPO_3$ can be stored over calcium chloride in a desiccator.

Physical Properties of Sodium Phosphate Melts

As is the usual case with inorganic, glass-forming melts, the molten sodium phosphates all exhibit Newtonian flow, so that at any given temperature, composition, and pressure, the flow is described by a single constant, the coefficient of viscosity. The viscosity data[65] are also found to fit the well-known relationship, $\eta = ae^{E/RT}$. Values for the activation energy for flow, E, for $1 < Na_2O/P_2O_5 < 2$ is given by the equation

$$\log E = -0.515\ (Na_2O/P_2O_5) + 4.722 \qquad (12\text{-}70)$$

Furthermore, the quantity, a, which is a function of the molar volume and the difference in entropy of the activated and initial states is given by a somewhat similar equation

$$a = 0.0298\ (Na_2O/P_2O_5)^2 - 0.0522\ (Na_2O/P_2O_5) + 0.0240 \qquad (12\text{-}71)$$

A plot of the logarithm of viscosity *vs.* reciprocal temperature for various compositions throughout the range of interest is given in Figure 12-24,

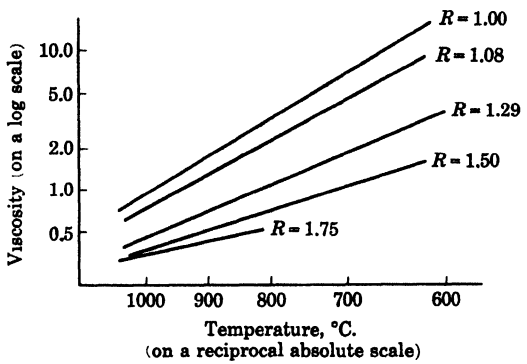


Fig. 12-24. Viscosity of Na_2O–P_2O_5 melts.

where it can be seen that the viscosities range from about $^1/_{10}$ poise to 10 poises. This means that these melts are quite viscous—about as syrupy as concentrated solutions of sugar—at the lower temperatures.

[65] C. F. Callis, J. R. Van Wazer, and J. S. Metcalf, *J. Am. Chem. Soc.*, **77**, 1471 (1955); also see K. Arndt, *Z. Chem. Apparatenkunde*, **3**, 549 (1908).

The densities and surface tensions of the liquids described above have also been measured.[66] The density of these melts usually lies in the range of 2.1–2.3 g./ml. Accurate values of the density can be determined from the following equation

$$d = 2.372 + 0.089\ (Na_2O/P_2O_5) - 0.000338t \qquad (12\text{-}72)$$

where d is the density in g./ml, Na_2O/P_2O_5 is the mole ratio, and t is the temperature in °C. of the melt. The surface tension of these melts—like the density—is also high, being approximately three times that of water. Under normal melt conditions, the surface tension will range from 150 to 300 dynes/cm. The equation for the surface tension is given below

$$\gamma = 150.6 - 0.379t + 67.7\ (Na_2O/P_2O_5) \qquad (12\text{-}73)$$

where γ is the surface tension in dynes/cm., t is the temperature in °C., and Na_2O/P_2O_5 is the mole ratio in the melt.

An apparent molecular weight for the molten sodium phosphates was estimated by putting the surface tension and density data into the Eötvös equation which was differentiated with respect to temperature. This led to an effective average molecular weight corresponding to about 12 phosphorus atoms in the molecule-ion. Similarly, the surface tension and density data can be used in the Macleod equation to give an apparent molecular weight equivalent to a monophosphate. The low molecular weights obtained for the melts probably represent a time-averaged size of the unit involved in the reorganization, with weighting of the smaller units. The viscosity data can also be used to obtain an approximate size of the flow unit according to the absolute theory of reaction rates.[67] For very short chain glasses, the flow unit is small, equivalent to one phosphorus atom. However, for melts corresponding to long chain glasses ($\bar{n} > 50$), the flow unit reaches a constant value corresponding to about eight phosphorus atoms. This group of eight phosphorus atoms may be the segment of a long chain which is involved in the flow or, on the other hand, it could represent an average size of the reorganization fragments in the melt.

At low temperatures, the molten phosphates are good absorbers of heat radiation, since 90% of the energy in the far infrared (>2.5 μ) is absorbed in a thickness of about 0.01 mm. of the melt. However, in the near infrared, the glass is considerably more transparent, with only about 62% of the

[66] C. F. Callis, J. R. Van Wazer, and J. S. Metcalf, *J. Am. Chem. Soc.*, **77**, 1468 (1955).

[67] A. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Co., New York, 1941. For details, see W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.*, **62**, 3113 (1940).

energy being absorbed in a thickness of 1 m. Radiation transfer of energy plays an important role not only in the absorption of heat by the melt but in the over-all thermal conductivity within the melt.[68]

Physical Properties of the Sodium Phosphate Glasses

Very few of the physical properties (such as tensile strength, refractive index, and elastic coefficients) which have been thoroughly investigated in

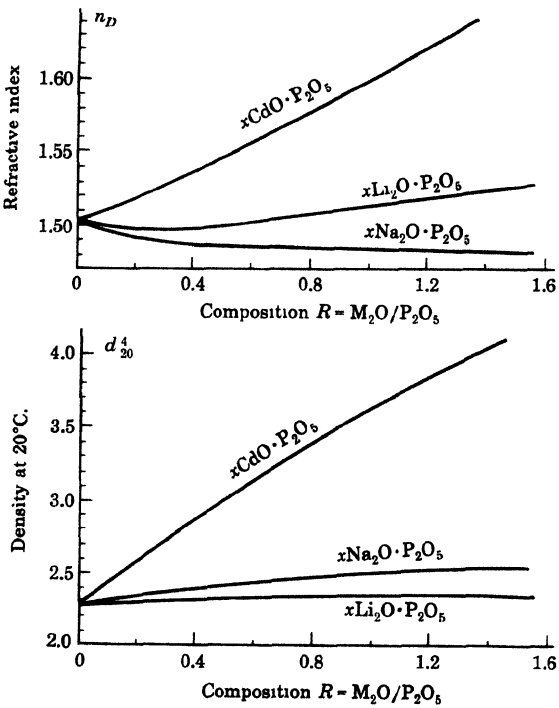


Fig. 12-25. Refractive index and density of several phosphate glasses as a function of composition.

the case of silicate glasses have been studied for phosphate glasses. However, measured values[69] of the refractive index and density of sodium phosphate glasses as a function of R are presented in Figure 12-25.

All of the sodium phosphate glasses lying between the metaphosphate

[68] B. S. Kellett, *Brit. J. Glass Technol.*, **36**, 115 (1952).

[69] E. Kordes and H. Becker, *Z. anorg. Chem.*, **260**, 13 (1949).

and tripolyphosphate compositions are soluble in water. The glasses for which the Na_2O/P_2O_5 mole ratio is greater than about 1.1 dissolve in well-stirred water about as rapidly as does sodium chloride or sugar, ground to the same particle size.[82] However, if these same glasses are added to water without stirring, they congeal together to form a sticky mass which is extremely slow to dissolve. This latter effect is attributable to the ability of the glasses to form extremely concentrated solutions of high viscosity, so that the particles are bound together into a partially hydrated mass exhibiting only a small surface area for further dissolution.

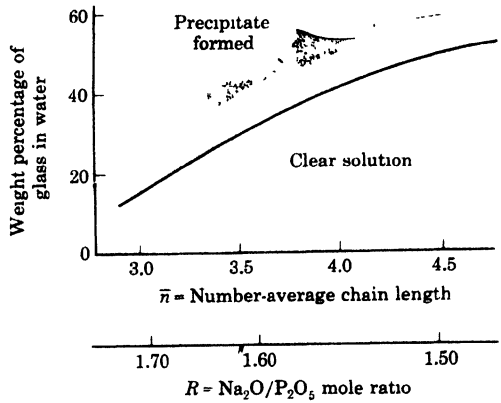


Fig 12-26 Region of composition and concentration at which sodium phosphate glasses form precipitates immediately after dissolution.

The sodium phosphate glasses containing long chain molecule-ions, for which $1.1 > Na_2O/P_2O_5 > 1.0$, dissolve slowly as do the other sodium phosphate glasses when the particles are allowed to congeal together in unstirred solutions. Moreover, even when the solutions are stirred, these glasses do not dissolve as rapidly as those corresponding to shorter chain lengths. Instead, their particles gradually hydrate to gelatinous masses which slowly become larger and more ill-defined and finally disappear into the solution. This over-all process of dissolution is followed no matter how fast the solution is agitated, and it can be observed visually because of the difference in the index of refraction between the gelatinous mass and the homogeneous liquid.

For glasses very near the tripolyphosphate composition ($1.5 < Na_2O/P_2O_5 < 1.7$), a precipitate is formed immediately upon dissolution in water, provided that the concentration is sufficiently high. The region of con-

centration and composition where this precipitate can be observed is given in Figure 12-26. This rapid formation of crystalline material in concentrated solutions of glasses near the tripolyphosphate composition can be readily observed by moistening a piece of the clear glass with a few drops of water. Usually a freshly dampened surface of sodium phosphate glass is completely transparent, but, in this case, the surface becomes cloudy. Then as the moisture permeates through the material, the depth of the cloudy layer increases until the entire piece is converted into a whitish mass. If a piece of such glass—which was originally hard, brittle, and transparent—

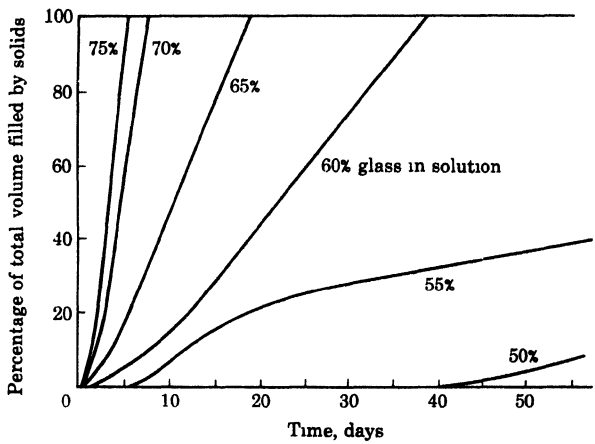


Fig. 12-27. Precipitation in aqueous solutions of a sodium phosphate glass ($Na_2O/P_2O_5 = 1.42$) which was allowed to stand at room temperature. Solutions containing less than 48% glass did not give a precipitate in three years.

is allowed to stand for several hours in contact with a relatively small amount of water, the piece will still retain its gross shape, although it becomes soft and plastic, with an opaque white appearance. Microscopic examination then reveals a mixture of fine, nonisotropic, crystalline particles in a viscid isotropic matrix. This precipitate is caused by crystallization of sodium pyro- and tripolyphosphates, since glasses in this range of composition contain a considerable proportion of these two phosphates, viz. Figure 12-9. Although glasses for which Na_2O/P_2O_5 is somewhat less than about 1.5 contain enough pyro- and tripolyphosphate ions to give a crystalline precipitate in extremely concentrated solutions, the high viscosity of such solutions inhibits the rate of formation of the crystal nuclei so that the clouding phenomenon is not observed in a reasonable time.

An interesting phenomenon, which is found for all of the glassy phosphates upon ageing, is related to the above-mentioned crystallization. When concentrated solutions of glassy phosphates stand for a number of months (with the exact time depending on the pH and temperature), there is a build-up of solid crystalline material. This is exemplified by the data

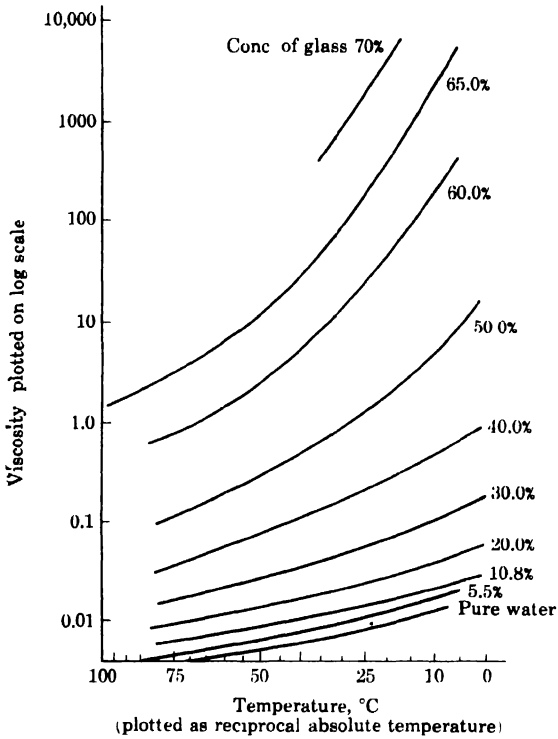


Fig. 12-28. Variation of viscosity (in poises) with temperature for a sodium phosphate glass for which $n = 4.9$

shown in Figure 12-27. As hydrolytic degradation proceeds, the concentrations of ortho-, pyro-, and tripolyphosphate ions build up to the point where crystals of the sodium salts of these materials finally start to precipitate. Thereafter, there is a gradual increase in the amount of the precipitate. After standing for a century or so, the concentrated solution of the phosphate glass will turn completely into a saturated solution of the equivalent sodium orthophosphates, with an amount of solid in contact with the

saturated solution depending on the Na_2O/P_2O_5 ratio of the starting glass and its concentration in solution.

Except for the glasses for which Na_2O/P_2O_5 mole ratio is greater than about 1.5, the glassy sodium phosphates appear to be miscible in all proportions with water. Naturally, the highly concentrated solutions will exhibit a tremendously high viscosity. In other words, in the system *sodium phosphate glass–water* there is a continuous increase in viscosity from that of water to that of the anhydrous glass as the sodium phosphate concentration

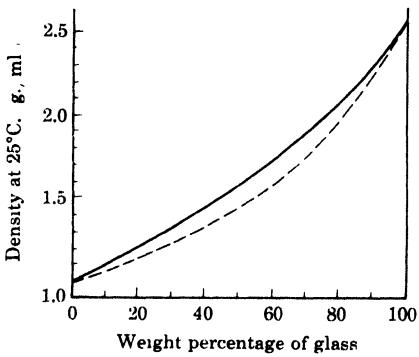


Fig. 12-29. Density of aqueous solutions of a phosphate glass for which = 4.9. The calculated curve is based on the assumption of no volume change on mixing the glass with the water

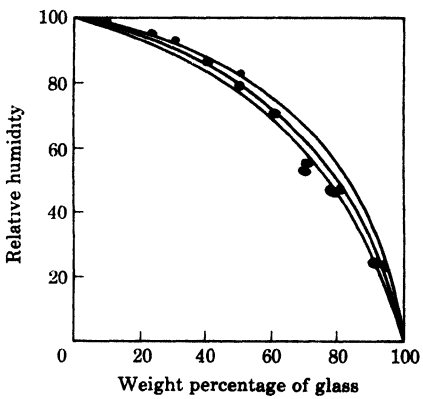


Fig. 12-30. Partial pressure of water vapor at 25° C. over aqueous solutions of a phosphate glass for which n = 4.9. Experimental data shown as points. Smooth curves calculated from Raoult's Law, assuming 60 (lowest curve), 70, and 80 g. of glass give 1 mole of dissociated particles. Assuming complete ionization, 70 g. of glass would have 1 mole total of ions

is increased. A plot of the temperature dependence of viscosity of the solution of a typical sodium phosphate glass as a function of concentration[70] is shown in Figure 12-28, from which it can be seen that the viscosity of a 70% solution at 25°C. is approximately a million times greater than that of pure water. All of these solutions exhibit Newtonian flow characteristics. As is usually the case,[71] the more viscous solutions exhibit the greatest change

[70] J. R. Van Wazer, *Ind. Eng. Chem.*, **41**, 189 (1949).

[71] J. R. Van Wazer, *Encyclopedia of Chemical Technology*, eds. R. E. Kirk and D. F. Othmer, Interscience Publishers, New York, 1953, Vol. XI, pp. 734–35.

of viscosity with temperature. Analysis of these flow data by the absolute theory of reaction rates[67] indicates that, up to a concentration of approximately 15–20% of dissolved glass, the flow units are water molecules and, above this concentration, the flow can be attributed to the motion of segments of the hydrated polyphosphate molecule-ions.

The density of aqueous solutions of the same sodium phosphate glass on which the viscosity determinations were made is shown in Figure 12-29 as a function of concentration. As might be expected for a binary system exhibiting strong molecular interaction, the total volume of a mixture of water and the sodium phosphate glass is less than the sum of the volumes of the two components. The partial pressure of water over solutions of this so dium phosphate glass has also been determined, and these data are presented in Figure 12-30. Since the average chain length of the anions in this glass was 4.9 phosphorus atoms, it can be calculated that 70 g. of the glass will contain 0.84 mole of sodium ion (assumed to be completely dissociated) and 0.16 mole of polyphosphate molecule-ions, or 1 mole of particles in all. The middle curve shown in Figure 12-30 corresponds to the partial pressure of water computed from Raoult's Law on the assumption that 70 g. of the glass contain 1 mole of the particles. In the more dilute solutions, the experimental points lie above the curve calculated on the basis of complete dissociation. This effect may be ascribed to the formation of polyphosphato-sodium complexes. A considerable amount of work has been done on the physical chemistry of dilute solutions of the vitreous sodium phosphates for which Na_2O/P_2O_5 lies between 1 and 1.5. This work has been reviewed[72] in the literature and is discussed on pages 471–477.

Graham's Salt and Its Hydrolysis

Because of the strong emphasis in the classical chemical literature on ortho-, pyro-, and metaphosphates, a great deal of effort has been devoted to Graham's salt—the sodium phosphate glass of the metaphosphate composition Because solutions of Graham's salt contain long chain phosphates, it is an especially good precipitating agent. The precipitates formed by adding heavy metal and alkaline earth salts to solutions of Graham's salt were studied by several investigators during the 19th century.[73] In general, there are two types of precipitates formed with Graham's salt: flocculant curds and viscous oils or jellies. Precipitates with silver, lead, barium, strontium, and mercurous salts are flocculant,

[72] C. F Callis, J. R. Van Wazer, and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954)

[73] For example, H Rose, *Ann. Physik*, **76**, 1 (1849); A. Ludert, *Z anorg. Chem.*, **5**, 15 (1894).

whereas the precipitates with copper, calcium, manganese, ferrous iron, nickel, and mercuric salts are oily or jelly-like. In general, there is about one atom of phosphorus in the precipitates for each equivalent of metal, regardless of the metal.

Like all other long chain phosphates and large polyanions in general, Graham's salt forms precipitates with cationic dyes and with proteins below their isoelectric points. It also precipitates a number of high molecular weight cations, such as quaternary amines containing long chain organic radicals. As is generally the case with chain phosphates, Graham's salt is a good complexing agent and also deflocculates and peptizes colloids.

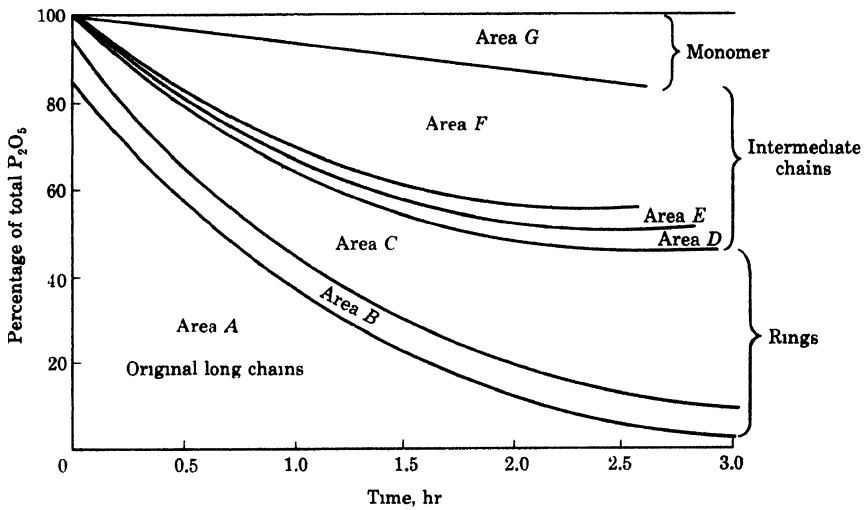


Fig. 12-31. Chromatographic results obtained by hydrolyzing Graham's salt at pH 4 and 90°C. Area *A* = long chain phosphates (nonmoving in the chromatogram); *B* = ring metaphosphates containing 4 to 6 phosphorus atoms; *C* = trimetaphosphate; *D* = pyrophosphate; *E* = tripolyphosphate; *F* = chain phosphates (polyphosphates) containing 4 to 15 phosphorus atoms plus any rings made up of more than 6 phosphorus atoms; and *G* = orthophosphate

The hydrolysis of Graham's salt is particularly noteworthy, in that small rings—primarily trimetaphosphate—are formed during the process of degradation of the long chains.[48,74] It has been pointed out by Thilo *et al.* that this formation of rings from chains is a very general process for long

[74] E. Thilo, *Chem. Technik*, **4**, 345 (1952); E. Thilo, G. Schultz, and E. M. Wichmann, *Z. anorg. u. allgem. Chem.*, **272**, 182 (1953); E. Thilo and W. Wieker, *ibid.*, to be submitted.

chain phosphates, occurring for Kurrol's salt, as well as for Graham's salt It appears that hydrolytic degradation in neutral and alkaline solution consists primarily of scission at the ends of long chains with concomitant formation of rings which are nearly all trimetaphosphate.[48] In acidic solution there is also some random scission along the chain. Rate constants for the hydrolysis of Graham's salt with respect to formation of orthophosphate and end groups are of the same order of magnitude as those for pyro- and tripolyphosphates under equivalent experimental conditions. Indeed, for the sodium salts in pure water, the initial degradation measured in this manner for the long chains of Graham's salt is somewhat slower at each pH value than the initial degradation of the pyro- and tripolyphosphates, except for pyrophosphate at pH 10 As is the usual case for hydrolysis of P -O--P linkages in condensed phosphates, the activation energies for the build-up of orthophosphate and the formation of end groups range near 26 kcal./mole of P -O P linkages

All of the various steps involved in the hydrolytic degradation of Graham's salt are acid-catalyzed. In addition, basic media catalyze the step whereby rings formed from the large chains undergo scission to give small chains. A plot showing the various intermediates formed during acidic hydrolysis of Graham's salt to orthophosphate is shown in Figure 12-31.

Properties of Sodium Phosphate Glasses in the Ultraphosphate Region

The main distinguishing feature of the sodium ultraphosphate glasses is that they are slowly soluble in water. The two limiting end members, Graham's salt and vitreous P_2O_5, do not dissolve nearly as rapidly as the short chain glasses in the polyphosphate region. However, the ultraphosphate glass corresponding to about $Na_2O \cdot 2\ P_2O_5$ dissolves several hundred times more slowly, taking about five days for complete dissolution in water. A plot of rate of dissolution *vs.* Na_2O/P_2O_5 mole ratio in the ultraphosphate region shows a smooth diminution in rate of dissolution as the $Na_2O \cdot 2\ P_2O_5$ composition ($R = 0.5$) is approached from either side.

It is interesting to note that particles of the ultraphosphate glasses do not stick together when placed in quiet water. However, these glasses are quite hygroscopic, taking the traces of water out of relatively dry air.

The properties of the sodium ultraphosphates are in accord with the idea that these glasses contain network structures which are held together by branching points. Apparently, stearic hindrance comes into play so that, at the composition corresponding to $Na_2O \cdot 2\ P_2O_5$, the branching points holding the structure together are protected the best from scission by the

water. For lower Na_2O/P_2O_5 ratios, the steric hindrance diminishes; and for higher ratios there is more hydrolysis because the chains readily untangle so as to expose the less frequent branching points, thus allowing them to undergo rapid scission.

Phosphate Glasses Containing Various Cations

Although the chemistry of the sodium phosphate glasses has been studied more carefully than that of any other phosphate glass, some work has also been done on phosphate glasses containing the other alkali metals: lithium, potassium, and cesium. In their gross solubility characteristics, these glasses are similar; however, there are considerable differences in the ease in which melts containing these various ions can be vitrified. Lithium phosphate melts are very similar to sodium phosphate melts, in that a continuous series of glasses ranging from pure P_2O_5 to compositions near $5\ LiO_2 \cdot 3\ P_2O_5$, can be made by the usual rapid chilling procedures. However, the potassium system is quite different in that clear glasses cannot be prepared in the region near the metaphosphate composition, $K_2O \cdot P_2O_5$ ($R = 1.0$), because of the rapid crystallization of potassium Kurrol's salt from the melt. A $K_2O \cdot P_2O_5$ melt cannot be made into a clear glass by the use of hand-operated chill plates—the chilled melt always appears cloudy and can be shown by x-ray diffraction to contain crystalline Kurrol's salt. The potassium ultraphosphate glasses are very readily prepared; and clear glasses in the range between about $11\ K_2O \cdot 10\ P_2O_5$ ($R = 1.1$) and $5\ K_2O \cdot 3\ P_2O_5$ ($R = 1.67$) can also be made. Cesium metaphosphate melts crystallize more readily than do the potassium melts, so that even on rapid quenching, a crystalline mass containing little or no glass is obtained.

On moderately slow cooling, crystalline masses are obtained from melts of lithium, potassium, and cesium metaphosphates but not from the sodium metaphosphate melt. In order to obtain crystalline sodium trimetaphosphate, it is necessary to temper the melt. This qualitative information on the relative rates of crystallization of the alkali metal metaphosphates emphasizes the fact that the ability to form glasses depends to a great extent upon the character of the crystals which can be grown from the melt, as well as on the properties of the melt itself. Thus, potassium Kurrol's salt crystallizes very readily, presumably because of the fortuitous way in which potassium ions can pack into crystals with the long polyphosphate chains. For further information on the crystals referred to here, see Chapter 10.

The ammonium phosphate glasses are extremely difficult to make without special equipment, because of the volatility of ammonia. However, in

the preparation of the reaction products of ammonia and phosphorus pentoxide (see Chapt. 13), vitreous ammonium phosphates have been made as byproducts.[75] These glasses are quite hygroscopic and usually exhibited a relatively low pH when dissolved in water—in the neighborhood of pH 4.

Melts of silver, calcium, cadmium, and lead phosphates are very readily cooled to a glass, and the available information indicates that the range in

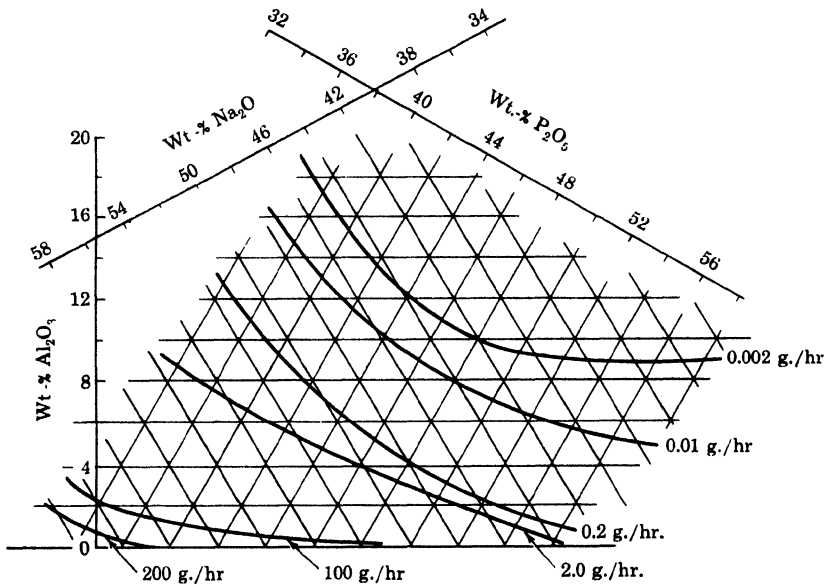


Fig. 12-32. A section of an Na_2O–Al_2O_3–P_2O_5 three-dimensional diagram showing rates of dissolution of vitreous compositions The dissolution rates were determined by placing 20 g. of screened particles (10–20 mesh) in 100 g. of well-agitated water.

which glasses are readily formed extends from pure P_2O_5 to an M_2O/P_2O_5 mole ratio near 1.67, the tripolyphosphate composition.[76] It is interesting to note that phosphoric acids can readily be made in vitreous form in the case of H_2O–P_2O_5 compositions ranging from pure P_2O_5 all the way down to slightly beyond the orthophosphate composition, $3\ H_2O \cdot P_2O_5$. In the

[75] P. G. Arvan, unpublished data obtained in the laboratories of the Monsanto Chemical Co.

[76] A. V. Kroll, *Z. anorg. Chem.*, **76**, 387 (1912); *ibid.*, **77**, 1 (1912); *ibid.*, **78**, 95 (1912); E. Kordes, *Z. anorg. u. allgem. Chem.*, **241**, 1 (1939); *Z. physik. Chem.*, **43**, 119 (1939); *ibid.*, **50**, 194 (1941).

phosphoric acids, it appears that hydrogen bonding aids glass formation even when the average chain length, $\bar{n}$, in the melt is as small as one or two Although the phenomenon has not been carefully investigated, phosphate melts of most metal ions are believed to exhibit rapid crystallization at values of R below the tripolyphosphate composition, $R = 1.67$.

Phosphate glasses containing multiply charged metal ions—either with or without singly charged ions, such as the alkali metals, exhibit the interesting property of slow solubility. Although no studies of this property have been reported in the scientific literature, it has been discussed rather thoroughly in patents.[77,78] In general, it is found that as the proportion of multiply charged metal ions (such as Mg, Ca, Ba, Sr, Zn, and Fe) is increased in phosphate glasses in which the main cationic constituent is sodium, the rate of solution of the glass is reduced. This is illustrated for glasses in the system Na_2O–Al_2O_3–P_2O_5 in Figure 12-32, which is a graphical interpretation of some work reported by King.[75]

Glasses Containing Phosphates with Other Anions

Thilo[79] has done work with mixed sodium arsenate-phosphate glasses, equivalent in composition to Graham's salt. As is the case with the crystalline sodium arsenate-phosphates,[79] these glasses decompose by scission of P—O—As linkages, when dissolved in water, to give sodium orthoarsenate and a mixture of condensed phosphates. The average chain length of the condensed phosphate studied in solution is a function of the As/P ratio, so that, with one mole of arsenic to four moles of phosphorus, the average chain length of the phosphate is somewhat less than four.

Mixed sodium sulfate-phosphate glasses have been prepared by adding various proportions of sodium sulfate to sodium phosphate melts near the metaphosphate composition or by exposing alkaline phosphate melts to gaseous SO_3.[80] There appears to be an ill-defined region of composition in the Na_2O–P_2O_5–SO_3 system of glasses in which the glasses are slowly soluble.[81] When equimolar mixtures of $NaHSO_4$ and Na_2HPO_4 are heated to-

[77] G. B. Hatch, U. S. Pats. 2,539,305 (1951), 2,601,395 (1952, assigned to Calgon); C. S. King, U. S. Pats. 2,370,473, 2,370,472 (1945, assigned to Blockson); E. P. Partridge, U. S. Pat. 2,365,489 (1944, assigned to Hall Labs.); O. Rice and G. B. Hatch, U. S. Pa t. 2,337,856 (1943, assigned to Hall Labs.); O. Rice, U. S. Pat. 2,304,850 (1942, assigned to Hall Labs.).

[78] C. S. King, U. S. Pat. 2,395,126 (1946, assigned to Blockson Chemical Company).

[79] E. Thilo and L. Kolditz, *Z. anorg. u. allgem. Chem.*, **278**, 122 (1955).

[80] P. Baumgarten and C. Brandenburg, *Ber.*, **72B**, 555 (1939); P. Baumgarten and H. Hennig, *ibid.*, **72B**, 1743 (1939).

[81] J. R. Van Wazer, unpublished studies.

gether, there is a low-temperature (<200°C.) reaction resulting in the formation of Na_2SO_4 and NaH_2PO_4. Moderately rapid quenching of the melt corresponding to this mixture results in a cloudy glass in which most of the sodium sulfate is present as crystallites.[82] Ion exchange studies on Na_2O–P_2O_5–SO_3 melts which were rapidly quenched indicate that some of the sulfate remains with the long chain phosphates and does not pass through the exchange column as quickly as does simple sodium sulfate.[83] Abnormally rapid hydrolysis, as evidenced by pH measurements, also gives support to the idea that P—O—S or S—O—S linkages are to be found in such sodium sulfate-phosphate glasses.

Some work has been done on mixed sodium silicate-phosphate[84] and sodium borate-phosphate glasses, as well as on glasses in the system[85] B_2O_3–SiO_2–P_2O_5. All of these glasses, similarly to the sodium sulfate-phosphate glasses, exhibit slow solubility over certain regions of composition. The problem of the chemical constitution of such glasses with mixed anions is worthy of considerable study. It should be noted that amorphous mixtures of phosphoric acid and sulfur trioxide have also been reported in the literature.[86]

Amorphous compositions made by adding boron trifluoride to phosphates have received some study. To condensed phosphoric acids, ranging in composition from $3\ H_2O \cdot P_2O_5$ to $H_2O \cdot P_2O_5$, about one mole of BF_3 can be added per mole of phosphorus.[87] Porcelain-like compositions (presumably a matrix of crystallites in glasses) have been reported where approximately one mole of BF_3 vapor was absorbed in one mole of K_3PO_4 or Na_3PO_4 to give a material melting below 400°C. Similar experiments were also carried out with sodium and potassium pyrophosphates. The Na_2O–P_2O_5–BF_3 system is worthy of additional investigation to see whether the BF_3 molecule can act as an end group for phosphate chains, as intimated by Baumgarten.[80]

[82] L. F. Audrieth, J. R. Mills, and L. E. Netherton, *J. Phys. Chem.*, **58**, 482 (1954).

[83] K. J. Shaver and J. G. Stites, "The Heteropolymeric System, Na_2O–P_2O_5–SO_3," *Paper at the 131st National Meeting of the American Chemical Soc., Miami, Florida, Apr. 9, 1957*

[84] A. G. Pincus, U. S. Pat. 2,434,674 (1948, assigned to American Optical Co.).

[85] W. F. Horn and F. A. Hummel, *Trans. Soc. Glass Technol.*, **39**, 113 (1955); W. J Englert and F. A. Hummel, *ibid.*, **39**, 121 (1955).

[86] R. H. Adie, *J. Chem. Soc.*, **59**, 230 (1891); *Chem. News*, **63**, 102 (1891).

[87] A. V. Topchiev and Ya. M. Paushkin, *Doklady Akad. Nauk, S.S.S.R.*, **58**, 1057 (1947)

Miscellaneous Glasses of Commercial Interest

A large number of vitreous compositions containing phosphates have been studied at different times and for different purposes by glass technologists. Some of this information has been briefly reviewed by Weyl and Kreidl.[88] The phosphate-containing glasses studied by glass technologists are all chosen so as to exhibit extremely slow rates of dissolution in water. Indeed, the rates are so low that some of the glasses can be considered as not dissolving at all, and others must be thought of as being only slowly leachable by water. It is interesting to note that, when phosphate glasses are leached with water, an acidic solution results, whereas ordinary silicate glasses give alkaline solutions. The waters obtained from leaching "insoluble" phosphate glasses contain phosphoric acids in parts per million quantities, whereas the leach waters from silicate glasses contain alkali metal ions due to exchange of hydrogen for the constituent alkali metal atoms, so that hydroxyl ions build up in the leach.

Examples of typical phosphate glasses of commercial interest are given in Table 12-5 The first property which attracted interest to the phosphates in the field of glass technology was an unusually high index of refraction for a given chromatic dispersion, as compared to the glasses based on silicates. Because of this property, Schott and coworkers[89] in Jena introduced the use of phosphate crown glasses in anastigmatic lenses. However, because of undesirable attack by moisture (lack of chemical durability), the optical phosphate glasses were abandoned shortly after their introduction in 1902 In recent years the chemical durability of phosphate glasses has been greatly improved (viz. items No. 3 and 4[90] in Table 12-5).

Another optical property which drew attention to the phosphate glasses is their high ultraviolet transmission The glass called Corex,[91] which was developed for this use, is practically a pure calcium metaphosphate with minor additions of B_2O_3, SiO_2, MgO, and Na_2O. An example of a glass[92]

[88] W. A. Weyl, *Chem. Eng. News*, **27**, 1048 (1949), N. J. Kreidl and W. A. Weyl, *J Am. Ceramic Soc.*, **24**, 372 (1941).

[89] H. Hovestadt, *Jena Glass and Its Scientific and Industrial Applications*, Macmillan Co., London, 1902.

[90] For example, A. G. Pincus, U. S. Pat. 2,716,069 (1955, assigned to American Optical Co.); K. H. Sun, U. S. Pat. 2,430,539 (1947, assigned to Eastman Kodak); G. F. Brewster, N. J. Kreidl, and T. G. Pett, *Trans. Soc. Glass Technol.*, **31**, 153 (1947).

[91] H. P. Hood, *Glass Ind.*, **7**, No. 12, 287 (1926).

[92] H. G. Grimm and P. Hoopert, U. S. Pats. 1,964,629 (1934), 2,100,391 (1937, assigned to I. G. Farbenindustrie); 2,227,082 (1940, assigned to W. H. Duisberg, New York); W. Kaufmann and E Bungartz, U. S. Pat. 2,031,958 (1936, assigned to I. G. Farbenindustrie); E D Tillyer, U S Pat 2,423,128 (1947, assigned to American Optical Co.)

TABLE 12-5
Some Typical Phosphate Glasses of Commercial Interest

Item no.	Noteworthy properties	Ref.	Mole percentage composition						
			Ag_2O	AlF_3	Al_2O_3	B_2O_3	BaO	BeF_2	CaO
1	Light phosphate crown. n_D = 1.5159, Abbe dispersion, ν = 70.0. Readily attacked by water vapor	89			11 3	5 0			
2	Barium phosphate crown. n_D = 1.5760, ν = 65.2 Readily attacked by water vapor.	89			2 1	6 1	37 4		
3	Phosphate crown containing fluoride. n_D = 1.389; ν = 81. Some surface staining in moist air.	90			1 2			53 2	
4	Phosphate crown containing fluoride n_D = 1.447; ν = 64. Resistance to moisture equivalent to a good optical glass.	90		0 7				37 5	
5	Corex glass High u v transmission Low chemical resistivity	91			0 5	6 2			43 0
6	High u v. transmission	88			30 0		20 0		
7	Good u.v. transmission. High resistivity toward attack by metal vapors Good resistance to moisture	92			24 6	9 7	27 2		1 5
8	u.v. Fluorescent glass. Converts the 2540 A. mercury line into ultraviolet radiation of 3000–4000 A.	94			8 2		36 5		
9	Low dielectric constant, ϵ = 1-5, high breakdown potential.	88			21 3	14 0	0 9		
10	Pink iron-containing glass	88,95			6 3				
11	Heat-absorbing glass.	88,95			9 7				
12	Dosimeter glass for x-rays and γ-rays Before irradiation, blue luminescence is excited by light at 2400 A., after radiation orange-red luminescence is excited by light at 3300 A.	98	14 1		8 4		7 5		
13	Radioactive radiation-absorbing glass Density = 6 58, n_D = 1 9929; ν = 21 9 Lead equivalent for 100 kv radiation = 0 578.	99							
14	High resistance toward hydrofluoric acid.	100			14 3				21.4

also showing high ultraviolet transmission but better chemical resistivity is given as item No. 7 in Table 12-5. Because of their transparency in the ultraviolet, phosphate glasses (especially those containing cerium) tend to remain transparent under conditions of high-energy radiation,[93] as in Atomic Energy installations.

Fluorescent glasses[94] of high efficiency have been made by introducing activators, such as Mn, U, Sn, Th, and Sb, into phosphate glasses.

[93] N. J. Kreidl, *Ind. Eng. Chem.*, **46**, 170 (1954).

[94] W. A. Weyl, *Trans. Soc. Glass Technol.*, **30**, 90 (1946); also, for examples, see J. G. Hooley, U. S. Pat. 2,393,469 (1946, assigned to Corning Glass) and W. Kaufmann, L. Eckstein, and K. Rosenberger, U. S. Pat. 2,042,425 (1936, assigned to I. G. Farbenindustrie).

TABLE 12-5 (*continued*)

Item no.	Mole percentage composition (*continued*)													
	CdO	Ce_2O_3	Fe_2O_3	K_2O	MgO	NaCN	NaF	Na_2O	P_2O_5	PbO	SiF_4	SiO_2	TiO	WO_3
1														
				14 8	11 5				57 4					
2														
									54 4					
3														
							29 7	6 1	9 8					
4														
								30 3	30 3		1 1			
5														
					1 1			0 8	45 2			3 2		
6				20 0					30 0					
7														
				9 0					16 0			9 0		
8														
		1 9							53 4					
9														
									63 8					
10			2 1				73 0		18 6					
11			2 5	15 5	13 5	0 8			58 0					
12														
				18 7					51 3					
13														
	2 0								36 9	43 7			2 5	14 9
14									64 3					

An entirely different property of phosphate glasses that has also received some attention is their dielectric behavior.[88] Most silicate glasses have dielectric constants lying between six and seven (pure silica has a dielectric constant of 3.8), whereas phosphate glasses can be made with dielectric constants between four and six. At the same time, these phosphate glasses exhibit a high resistance to electrical breakdown.

In silicate glasses, ferric iron exhibits its usual brown coloration, which can be quite dark, as in brown bottles. In phosphate glasses,[95] the iron

[95] G. F. Brewster and N. J. Kreidl, *Trans. Soc. Glass Technol.*, **35**, 332 (1951); K. H. Sun and T. E. Collier, U. S. Pat. 2,496,824 (1950, assigned to Eastman Kodak).

usually exhibits a faint pink color. Glasses containing ferrous iron are a convenient means for filtering out the near infrared of strong light sources. Heat filters of this type based on silicate glasses exhibit a bluish green coloration because the absorption band of the ferrous iron in these glasses extends into the visible region However, colorless heat-absorbing glasses can be made with phosphates.[96] In these glasses, the absorption band is shifted so as to lie completely in the infrared region for FeO concentrations as high as 2–3%. Indeed, phosphate-based glass compositions can be made which absorb both ultraviolet and infrared radiation but have a high transmission in the visible range of the spectrum.[97] These effects with both ferrous and ferric iron are probably all related to the complexing ability of the phosphates discussed on pages 459–468

Some of the solvent properties[85] of phosphate melts have been of considerable interest to glass technologists Thus, phosphate glasses can dissolve silica to a considerable extent, whereas silicate glasses do not dissolve phosphates in appreciable quantities Furthermore, phosphates can dissolve large amounts of fluoride, such as CaF_2, without turning opaque on cooling, as is the case with silicate glasses. Silver in silicate glasses is easily reduced to precipitate metallic silver. However, more than 10% Ag_2O can be dissolved in phosphate glasses without giving rise to color or precipitation! This property forms the basis of a γ-ray-sensitive glass which is converted by irradiation to a phosphor.[98] If, after exposure to γ-rays, the glass is viewed under ultraviolet light, it emits visible light, the intensity of which is proportional to the γ-ray dosage The fluorescence is probably due to neutral silver atoms formed by reduction of silver ions during the γ-ray exposure.

Another group of phosphate glasses,[99] also employed in the atomic energy field, is based on the $PbO–WO_3–P_2O_5$ system. Glasses in this stystem show an unusually high x-ray and γ-ray absorption and are not readily discolored by exposure to x-rays.

[96] A. G. Pincus, U. S. Pat. 2,359,789 (1944, assigned to American Optical Co.); E. Berger, U. S. Pat. 1,961,603 (1934), 2,194,784 (1940, assigned to Jenaer Glaswerk Schott).

[97] E. D. Tillyer, H. R. Moulton, and T. M. Gunn, U. S. Pat. 2,226,418 (1940), 2,278, 501 (1942, assigned to American Optical Co.).

[98] J. H. Schulmann, R. J. Ginther, and L. W. Evans, U. S. Pat. 2,524,839 (1950, assigned to U. S. Govt.); W. A. Weyl, J. H. Schulmann, R. J. Ginther, and L. W. Evans, *J. Electrochem. Soc.*, **95**, 70 (1949), J. H. Schulmann, R. J. Ginther, C. C. Klick, R. S. Alger, and R. A. Levy, *J. Applied Phys.*, **22**, 1479 (1951).

[99] J. J. Rothermel, K. H. Sun, and A. Silverman, *J. Am. Ceramic Soc.*, **32**, 153 (1949); A. Silverman, J. J. Rothermel, and K. H. Sun, U. S. Pat. 2,518,194 (1950).

Replacement of oxygen by sulfur is not possible in the usual soda-lime-silicate glasses because oxidation and polymerization of the sulfur ions lead to colored polysulfides. In addition, traces of heavy metals, such as lead or iron, in these glasses give dark-colored metal sulfides. Phosphate glasses are good solvents for sulfides, presumably because of the formation of thiophosphates (see Chapt. 13). The presence of sulfur as a relatively stable thiophosphate made it possible to melt a phosphate mixture containing appreciable amounts of both sulfur and lead to give a colorless glass on quenching.[88] Sulfur in phosphate glasses produced adhesion between these glasses and metal surfaces.[88]

Since phosphorus does not form a volatile fluoride in the presence of moisture and/or oxygen as does silicon, phosphate glasses are resistant to hydrofluoric acid. Such fluorine-resistant glasses have been used for laboratory ware.[100] It is interesting to note that phosphate glasses are usually resistant to HF but are somewhat attacked by H_2O, whereas with equivalent silicate glasses the reverse is true.

Esters of Condensed Phosphoric Acids

At the present time there is little conclusive experimental evidence to show that condensed phosphate esters should be included in this chapter on reorganizing phosphates; but, on the other hand, there is also no evidence to show that they should not be. These esters are briefly reviewed by Kosolapoff,[101] who discusses them primarily in terms of the classical pyro-meta notation. A material called "hexaethyl tetraphosphate"[102] was made by reacting one mole of $POCl_3$ with three moles of triethyl phosphate. This substance has been studied in a number of industrial laboratories and is shown to be a mixture of condensed phosphates.

Ill-defined metaphosphate esters have been described in a number of different articles.[101] Thus, ethyl metaphosphate has been made by thermal decomposition of tetraethyl pyrophosphate into triethyl orthophosphate and ethyl metaphosphate.[103] It has also been prepared by reacting ethanol with phosphorus pentoxide;[104] from the thermal decomposition of di-

[100] E. C. Buck, U. S. Pat. 1,570,202 (1926); L. Knaffi, U. S. Pat. 295,410 (1884).

[101] G. M. Kosolapoff, Organophosphorus Compounds, John Wiley & Sons, Inc., New York, 1950, Chapt. 12, pp. 333-54

[102] G. Schrader, Ger Pat 720,577 (1942). U. S. Pat. 2,336,302 (1943, assigned to I. G. Farbenindustrie); S A Mumford and E A. Perren, *Bios. Report No. 1108* [O.P.B. Report 87923-R] (1945)

[103] D. Balareff, *Z. anorg. u. allgem. Chem.*, **99**, 187, 190 (1917); *ibid.*, **101**, 225 (1917).

[104] K. Langheld, *Ann.*, **43**, 1857 (1910). *ibid.*, **44**, 2076 (1911); *ibid.*, **45**, 1125, 3737, 3760 (1912); W Steinkopf and I Schubart, *ibid.*, **424**, 1 (1921).

ethyl chlorophosphate;[103] and by reacting triethyl phosphate with phosphorus pentoxide.[105] An interesting review of the chemistry of ethyl metaphosphate, as well as some original contributions to this chemistry, is given by Rätz and Thilo.[106] However, it is believed that the relatively simple structure suggested by these authors is incorrect, and that the so-called "ethyl metaphosphate" is a complicated mixture. Nuclear magnetic resonance data[107] have been tentatively interpreted to show that a crude preparation of "ethyl metaphosphate" made by reacting ether with phosphorus pentoxide contained about 25% of the total phosphorus as end units, 72% as middle units, and 3% as branching units.

Long chain phosphates have been identified in yeasts, molds, algae, and bacteria.[108] It is believed that these long chain phosphates occur, at least to some small extent, as organic derivatives. An interesting enzymatic synthesis of the long chain phosphate salts (not esters or other organic derivatives) has been described.[109] According to this, the polymerization is believed to occur by donation of the terminal PO_4 group of adenosine triphosphate to the growing chain.

[105] H. Alder and W. H. Woodstock, *Chem. Ind.*, **51**, 516 (1942); W. H. Woodstock, U. S. Pat. 2,402,703 (1946, assigned to Victor Chem. Works).

[106] R. Ratz and E. Thilo, *Ann.*, **572**, 173 (1951).

[107] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

[108] E. Thilo, H. Grunze, J. Hammerling, and G. Werz, *Z. Naturforsch.*, **11b**, 266 (1956) (algae); J. P. Ebel, *Compt. rend.*, **288**, 1312 (1949) (corynebacteria); G. Schmidt, L. Hecht, and S. J. Thannhauser, *J. Biol. Chem.*, **178**, 733 (1949); *ibid.*, **166**, 775 (1946); J. M. Wiame, *Bull. soc. chim. biol.*, **28**, 552 (1946) (yeast); B. Ingelman and H. Malmgren, *Acta Chem. Scand.*, **4**, 478 (1950); B. Ingleman, *ibid.*, **1**, 776 (1948); *Svensk. Kem. Tidskr.*, **60**, 222 (1948) (mold).

[109] A. Kornberg, S. R. Kornberg, and E. S. Sims, *Biochim. et Biophys. Acta*, **20**, 215 (1956).

CHAPTER 13

Halo-, Peroxy-, Thio-, and Amidoacids of Phosphorus, Their Salts, Esters, and Related Compounds

INTRODUCTION

In the phosphorus-based anions described in Chapters 7 through 12, the phosphorus atom is quite generally surrounded by four other atoms which may be either hydrogen, carbon, oxygen, or other phosphorus atoms. The acids corresponding to these anions are so formulated that one to three oxygen atoms per phosphorus are situated in hydroxyl radicals, the hydrogen of which is usually dissociated. In ester formation, these hydrogens are replaced by organic radicals; and, in all of the esters corresponding to the structures described above, the phosphorus is quadruply connected to its neighboring atoms. However, there are a few esters in which the phosphorus is triply connected. Acids and salts corresponding to the esters having triply connected phosphorus atoms are not known, since a hydrogen of such acids migrates so as to be a fourth atom attached to the phosphorus.

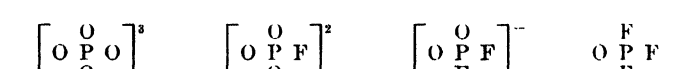
In the peroxyacids of phosphorus and their derivatives described in this chapter, one or more of the oxygens attached to the phosphorus are also attached to another oxygen atom, so that there is at least one P—O—O linkage in the structure of the molecule or ion. Thioacids and their derivatives are formed by substituting sulfur atoms for some or all of the oxygens; whereas, in the amido- or halo acids and their derivatives, a nitrogen or a halogen atom is attached directly to the phosphorus, with the acid function still coming from a dissociated hydrogen of a —SH or —OH group. In other words, the majority of the compounds described in this chapter differ from the compounds described in Chapters 7 through 12 in that there is a halogen, sulfur, and/or nitrogen atom or a peroxy linkage attached directly to the phosphorus. In addition to these compounds which are the main topics of this chapter, there are also discussed the hexafluorophosphate anion and some miscellaneous acid derivatives in which such elements as selenium and tin are directly connected to the phosphorus.

Most of the work on the compounds discussed here has been carried out

during the late 19th and early 20th centuries. Exceptions to this are the studies of Gladstone[1] on phosphoramidates in the middle of the 19th century and the even earlier preparation by Berzelius[2] of a thiophosphate in 1843. No particular author's name is associated with most of the classes of compounds described in this chapter. However, there are exceptions in the case of Lange,[3] who discovered the fluorophosphoric acids and has made the major contribution to their elucidation, and in the case of Stokes,[4,5] who made important contributions to the understanding of the nitrogen-containing acids of phosphorus.

THE HALOACIDS AND THEIR DERIVATIVES

By substituting fluorine atoms for oxygen atoms in the orthophosphate anion, the following series is obtained



(13-1)

The first member of this series, the orthophosphate anion, is described in considerable detail in Chapter 9, whereas the last member, the neutral phosphoryl fluoride, is discussed in Chapter 5. The second member of this series is the monofluorophosphate anion, and the third member is the difluorophosphate anion. As is the case with neighboring elements, phosphorus forms halogenated anions with fluorine which are stable in aqueous solution. However, by substituting alkoxy or aroxy groups for some of the halogen atoms in phosphorus trichloride or tribromide or in phosphoryl chloride or bromide, a number of un-ionized compounds are obtained which are formally classed as esters. These compounds are discussed in this section, along with the inorganic compounds based on the fluorophosphate anions.

Because of the high electronegativity of fluorine, phosphorus pentafluoride can combine with a fluoride ion to form the hexafluorophosphate anion, PF_6^-, in which the phosphorus is present as an sp^3d^2-hybrid. This

[1] J. H. Gladstone, *J. Chem. Soc.*, **2**, 131 (1850); **3**, 135, 353, 3153 (1851); **22**, 15 (1869); J. H. Gladstone and J. D. Holmes, *ibid.*, **17**, 225 (1864); **18**, 7 (1865); **19**, 1 (1866); **21**, 64 (1868); *Proc. Roy. Soc. (London)*, **15**, 510 (1867); *Chem. News*, **9**, 260 (1864); **12**, 282 (1865).

[2] J. J. Berzelius, *Ann.*, **46**, 254 (1843).

[3] A recent review is given by W. Lange, *Fluorine Chemistry*, ed. J. H. Simons, Academic Press, New York, 1950, Vol. I, Chapt. 3, pp. 138–67.

[4] H. N. Stokes, *Am. Chem. J.*, **15**, 198 (1893); *ibid.*, **16**, 123 (1894).

[5] H. N. Stokes, *Am. Chem. J.*, **18**, 629, 780 (1896); *ibid*, **20**, 740 (1898).

strongly ionized anion is somewhat similar to the hexafluorosilicate anion, SiF_6^{2-}. However, as might be expected, the hexafluorophosphate anion is the more stable of the two. It should be noted that arsenic and antimony also form hexafluoro anions, AsF_6^- and SbF_6^-. The hexafluoroarsenate anion is about as stable[5a] as the hexafluorophosphate anion, whereas the SbF_6^- anion hydrolyzes rapidly upon dissolution in water.

The fluorophosphoric acids are transformed into one another with comparative ease. In addition, they are found to form readily even when substantial quantities of water are present. Details of this will be discussed below under the individual acids. However, the over-all reaction scheme[6] showing the relationships between the fluorophosphoric acids and orthophosphoric acid is given below.

$$H_3PO_4 \underset{H_2O}{\overset{HF}{\rightleftharpoons}} H_2PO_3F \underset{H_2O}{\overset{HF}{\rightleftharpoons}} HPO_2F_2 \underset{2\,H_2O}{\overset{4\,HF}{\rightleftharpoons}} HPF_6 \qquad (13\text{-}2)$$

Preparation of Hexafluorophosphates[3,6]

The original preparation of a hexafluorophosphate was made by precipitating the slightly soluble nitron salt of the hexafluorophosphate anion from the reaction product of aqueous hydrofluoric acid with phosphorus pentoxide.[7] However, the yield is very small; for example, there is only 0.4% of this acid in the mixture obtained by combining P_2O_5 with aqueous 40% HF. Probably the best preparation of ammonium and alkali metal hexafluorophosphates is achieved by combining the chloride salt of the cation with phosphorus pentachloride in anhydrous liquid hydrogen fluoride.[8] The reaction is carried out in a stainless steel, nickel, or Monel vessel, chilled in an ice-salt bath. The desired chloride is dissolved in the anhydrous hydrogen fluoride, and then the phosphorus pentachloride is slowly sifted into the solution. Although the resulting hexafluorophosphate begins to precipitate immediately, the vessel is transferred to an oil bath where it is heated to about 150°C. to remove the last traces of hydrogen fluoride. The yields from this reaction are substantially theoretical, and the purity of the prod-

[5a] H. M. Dess and R. W. Parry, *J. Am. Chem. Soc.*, **79**, 158 (1957); and E. L. Muetterties and W. D. Phillips, *ibid.*, **79**, 3686 (1957).

[6] W. E. White, *Encyclopedia of Chemical Technology*, eds. R. E. Kirk and D. F. Othmer, Interscience Publishers, New York, 1951, Vol. VI, pp. 711–21.

[7] W. Lange, *Ber.*, **61B**, 799 (1928); W. Lange and E. Müller, *ibid.*, **63B**, 1058 (1930).

[8] M. M. Woyski, *Inorganic Syntheses*, ed. L. F. Audrieth, McGraw-Hill Book Co., New York, 1950, Vol. III, pp. 111–17.

ucts is well in excess of 95%. The equation for the reaction in the case of the sodium salt is given below.

$$NaCl + PCl_5 + 6\,HF \longrightarrow NaPF_6 + 6\,HCl \text{ (in excess liquid HF)} \quad (13\text{-}3)$$

Purification of sodium hexafluorophosphate is carried out by dissolving 60 g. of the salt in 100 ml. of methanol, adding a small amount of sodium hydroxide to make the solution permanently alkaline and thereby precipitating the iron impurities, centrifuging to remove impurities, and, finally, crystallizing under reduced pressure. The product from this sequence of reactions is the monohydrate which can be converted to the anhydrous salt by drying over sulfuric acid. Since NH_4PF_6 forms a double salt with NH_4F, the ammonium salt is not readily purified. Recrystallization will remove the ammonium fluoride only if the initial mixture contains less than about 1% NH_4F. Since the potassium salt is much less soluble in cold water than either the sodium or ammonium salt, it is easily purified by recrystallization through cooling of a hot aqueous solution.

Another reaction[9] which has been used to make hexafluorophosphates is heating phosphorus pentachloride with an alkali metal fluoride to 80–110°C. The over-all reaction is exemplified by the following equation.

$$6\,NaF + PCl_5 \longrightarrow NaPF_6 + 5\,NaCl \quad (13\text{-}4)$$

Isolation of the hexafluorophosphate ion is carried out by dissolving the reaction product in water and precipitating the nitron salt. This salt, in turn, is transformed into the ammonium salt by treatment with aqueous ammonia. Insoluble salts of the hexafluorophosphate anion are obtained by a metathesis reaction between a soluble salt of the metal and sodium or ammonium hexafluorophosphate.

A good procedure[6] for preparing hexafluorophosphoric acid is to react phosphorus pentoxide with anhydrous hydrogen fluoride in accordance with the following equation.

$$12\,HF + P_2O_5 \longrightarrow 2\,HPF_6 + 5\,H_2O \quad (13\text{-}5)$$

In order to avoid volatilization of the reactants, the reaction is carried out in a closed system with considerable cooling. Silver or aluminum equipment is used. The theoretical concentration (76.5 wt.-%) of hexafluorophosphoric acid is not reached because of the hydrolysis equilibria shown in equation 13-2, which leads to the formation of other fluorophosphoric acids and uncombined hydrofluoric as well as a small amount of orthophosphoric acid. A commercial sample of concentrated hexafluorophosphoric acid has been reported[6] to consist of 65 wt.-% HPF_6, 6 wt.-% HF, 21 wt.-%

[9] W. Lange and G. von Krueger, *Ber.*, **B65**, 1253 (1932).

H_2O, and 8 wt.-% of a mixture of HPO_2F_2, H_2PO_3F, and H_3PO_4. The hexahydrate of hexafluorophosphoric acid, $HPF_6 \cdot 6\ H_2O$, which melts at about 31.5°C., has been isolated in good yield by adjusting the water content to the proper concentration in a product containing a high percentage of HPF_6 and simultaneously cooling to low temperatures to avoid reaching equilibrium between the added water and the original mixture of fluorophosphoric acids. From the reaction product of hydrogen fluoride and 100% orthophosphoric acid, the hexahydrate may be obtained directly without the addition of water, *i.e.*, by simply cooling.

Nitrosyl hexafluorophosphate, $NO(PF_6)$, has been made by reacting $NO(SbCl_6)$ with $(CH_3)_4NPF_6$ in liquid sulfur dioxide.[10] Nitrosyl hexafluorophosphate has also been prepared by reacting nitrosyl chloride, NOCl, with phosphorus pentabromide in bromine trifluoride.[11] Nitryl hexafluorophosphate has been reported as being formed by reacting nitrogen dioxide, N_2O_4, with phosphorus pentabromide in BrF_3. Bromine trifluoride can also be used in making other fluorophosphates by adding mixtures of phosphorus pentabromide and metal halides to it.[11]

Structure and Properties of Hexafluorophosphates[3,6]

The crystal structure of potassium hexafluorophosphate has been worked out in considerable detail,[12] and it has been shown that ammonium, cesium, sodium, and thallium hexafluorophosphates exhibit the same anion as does α-KPF_6. In addition, the crystal structures of $NaPF_6 \cdot H_2O$ and $HPF_6 \cdot 6\ H_2O$ have also been determined.[13] In α-KPF_6 the potassium and phosphorus atoms form a lattice of the sodium chloride type, with the fluorine atoms being arranged octahedrally around the phosphorus atoms. At room temperature, the PF_6^- ions of the cubic α-form oscillate around the cell diagonal, while at −40 to −50°C., the oscillations are frozen. At an equilibrium temperature[14] of −15.6°C., the α-form transforms into a rhombohedral β-form of the barium hexafluorosilicate type. In $HPF_6 \cdot 6\ H_2O$, the water molecules form a cuboctahedral cage of 24 oxygen atoms, presumably held together by hydrogen bonds, in the center of which the phosphorus atom of the PF_6^- ion is situated. This arrangement is shown in Figure

[10] F. Seel and T. Gössl, *Z. anorg. u. allgem. Chem.*, **263**, 253 (1950).

[11] A. A. Woolf, *J. Chem., Soc.*, **1950**, 1053; A. A. Woolf and H. J. Emeléus, *ibid.*, **1950**, 1050; *ibid.*, **1950**, 164.

[12] H. Bode and H. Clausen, *Z. anorg. u. allgem. Chem.*, **265**, 229 (1951); H. Bode and G. Teufer, *ibid.*, **268**, 20 (1952); *ibid.*, **268**, 129 (1952).

[13] H. Bode and G. Teufer, *Acta Cryst.*, **9**, 825 (1956); *ibid.*, **8**, 611 (1955).

[14] O. Hassel and J. A. Hveding, *Arch. Math. Naturvidenskab*, **45**, No. 2, 1 (1941).

13-1. Again, the fluorine is arranged hexagonally around the phosphorus atom with the P-F distances being equal to 1.73 A. The most detailed structure study has been carried out on $NaPF_6 \cdot H_2O$, in which four fluorine atoms arranged at the corners of a square in the same plane as the phosphorus atom are found to be separated from the phosphorus by 1.58 A. The two remaining fluorine atoms are situated directly above and below the phosphorus on an axis perpendicular to the square formed by the four other

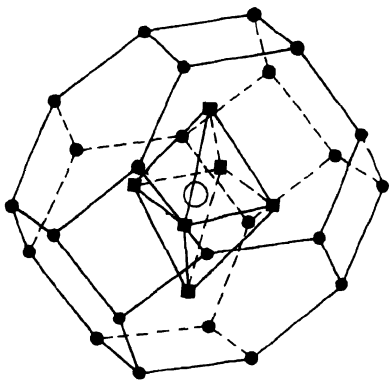


Fig. 13-1. Diagrammatic sketch of the cuboctrahedral cages of oxygen atoms around each hexafluorophosphate ion in the crystal of $HPF_6 \cdot 6H_2O$ The oxygen atoms are probably held together by hydrogen bonds. O = phosphorus atom of the PF_6^- ion; ■ = fluorine atoms of the PF_6^- ion; ● = oxygen atoms of the water

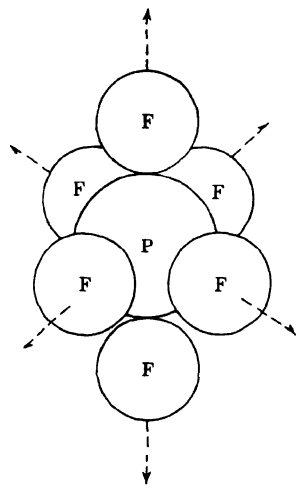


Fig. 13-2. The hexafluorophosphate anion

fluorine atoms. For these apical fluorines, the P-F distance was found to be 1.75 A. These distances are quite close to the calculated σ-bond distances, corrected for ionic effects of 1.63 ± 0.02 A. An unsophisticated interpretation of the measured distances indicates a small amount of π-character in the planar bonds, with the apical bonds exhibiting no π-character as well as a deficiency in σ-character. As was the case for the PCl_5 molecule and for the PCl_6^- ion found in crystalline PCl_5, the apical distances are somewhat larger than the other atom-center distances.

The symmetry and atom-center distances of the PF_6^- ion, as found from these crystal studies, correspond to those expected for phosphorus having an sp^3d^2 σ-bond base structure. The covalent character of the six bonds in this structure, which is shown in Figure 13-2, is demonstrated by nuclear

magnetic resonance studies[15] in which it is found that the fluorine atoms exhibit a doublet pattern, and the phosphorus atom exhibits a 1-6-15-20-15-6-1 septuplet resonance pattern —with the splitting into multiplets in both cases being due to indirect spin-spin coupling between the fluorine and the phosphorus. The phosphorus spectrum is shown in Figure 13-3.

The hexafluorophosphate anion titrates as a strong acid. Its electrical conductivity also corresponds to that of a strong electrolyte.[16]

There is an interesting solubility relationship between the hexafluorophosphates and the corresponding perchlorates, in that difficultly soluble

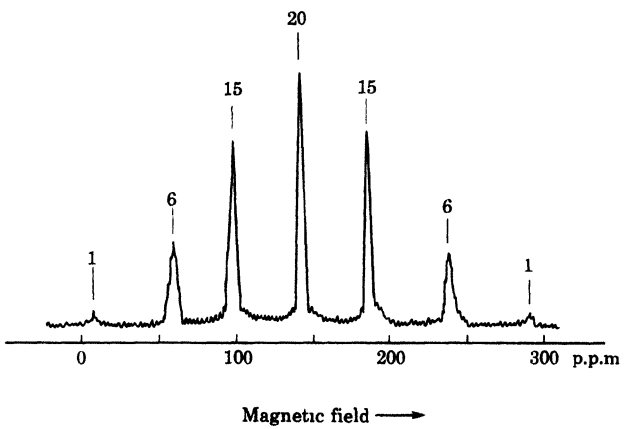


Fig. 13-3. Nuclear magnetic resonance of phosphorus in a pure sample of hexafluorophosphoric acid. The figures over the individual resonance peaks represent the theoretical intensities. The applied magnetic field was 9400 gauss, and the scale is given in parts per million of this field with respect to phosphoric acid as a standard.

hexafluorophosphates correspond to difficultly soluble perchlorates, as shown in Table 13-1. A number of hexafluorophosphates are exceedingly soluble in water. This includes the sodium and the ammonium salts. As previously mentioned, the ammonium hexafluorophosphate forms a double salt with ammonium fluoride, $NH_4PF_6 \cdot NH_4F$. The alkaline earth metal hexafluorophosphates are quite soluble in water, with the solutions exhibiting the usual stability of the hexafluorophosphate anion. However, upon evaporation— even at ice temperatures—hydrolysis occurs when the solutions approach saturation. This behavior also occurs to some extent with

[15] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); also D. Ames, C. F. Callis, and J. R. Van Wazer, unpublished results.

[16] I. Johnson and D. G. Rands, *Proc. Okla. Acad. Sci.*, **33**, 221 (1952).

TABLE 13-1
Solubilities of Some Hexafluorophosphates and Perchlorates in Water at Room Temperature (20°C.)

Cation	Solubilities in moles/l.	
	Hexafluorophosphates	Perchlorates
Potassium, K^+	0 432	0 120
Rubidium, Rb^+	0 076	0 071
Cesium, Cs^+	0 030	0 084
Hexammononickel, $[Ni(NH_3)_6]^{2+}$	0 0018	0 0069
Tetramethylammonium, $(CH_3)_4N^+$	0 0077	0 0652
Tetraethylammonium, $(C_2H_5)_4N^+$	0 0294	0 1056
Phenyldiazonium, $(C_6H_5)N_2^+$	0 036	0 070
Pyridine, $C_5H_5NH^+$	0 180	0 530
Strychnine, $C_{21}H_{22}O_2N_2H^+$	0 0033	0 0040
Brucine, $C_{22}H_{26}O_4N_2H^+$	0 0034	0 0054
Nitron, $C_{20}H_{16}N_4H^+$	0 0002	0 00005

the sodium salt. Although the solubility behavior of hexafluorophosphates is very similar to that of the perchlorates, the salts do not show crystallographic similarity. Thus, alkali metal perchlorates are rhombic at room temperature, whereas the hexafluorophosphates appear as cubes or rectangular plates As previously noted, the alkali metal hexafluorophosphates crystallize in the same system as sodium chloride. Therefore, when a drop of their aqueous solution is evaporated on fresh mica cleavage surfaces,[17] oriented growth (epitaxy) is exhibited. The solubility of potassium hexafluorophosphate[18] is shown in Figure 13-4.

Sterols containing the 3(β)-hydroxy-Δ^5-ene group are precipitated instantaneously from sufficiently concentrated chloroform solutions in the form of well-crystallized, colorless hexafluorophosphate salts, when hexafluorophosphoric acid (60–70% HPF_6) is added.[19] This behavior is nearly identical to that of concentrated perchloric acid. When the sterols are precipitated with an excess of the hexafluorophosphoric or perchloric acid, there is a slow reaction between the free mineral acid and the sterol to give halochromic compounds, so that a pronounced purple color appears in the solution. The addition of water hydrolyzes these compounds instantly, and the color disappears.

At room temperature the alkali metal hexafluorophosphates are rela-

[17] H. Seifert, *Z. Krist.*, **76**, 455 (1931); L. Royer, *Compt. rend.*, **191**, 1346 (1930).
[18] J. N. Sarmousakis and M. J. D. Low, *J. Am. Chem. Soc.*, **77**, 6518 (1955).
[19] W. Lange, R. G. Folzenlogen, and D. G. Kolp, *J. Am. Chem. Soc.*, **71**, 1733 (1949).

tively inert compounds which can be stored in glass if the containers are well sealed. However, over an extended period of time the action of moist air causes some hydrolysis to give hydrogen fluoride, which will, naturally, cause etching of glass. It is interesting to note that ammonium hexafluorophosphate fluoride sublimes at 140°C. Although the solid does not attack glass, the vapor does, since it is probably at least partially dissociated into hydrogen fluoride.

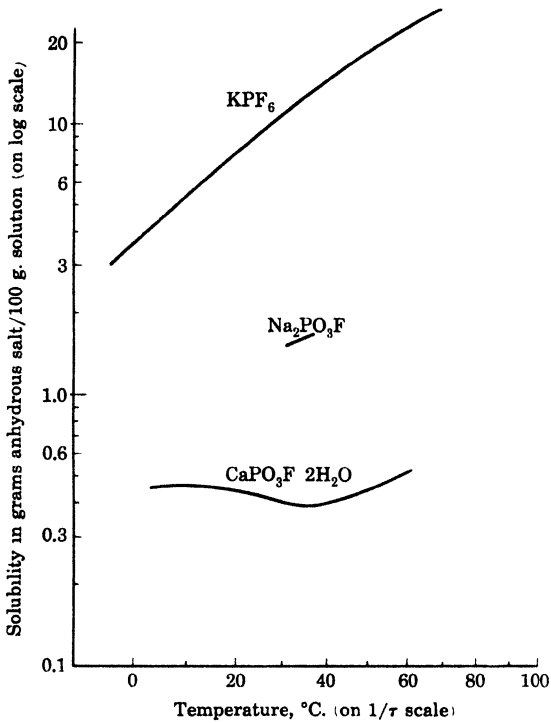


Fig. 13-4. Solubilities of several fluorophosphates. The value for Na_2PO_3F is only approximate.

When the dry alkali metal hexafluorophosphates are heated at high temperatures, they decompose. On the other hand, when dry alkali metal fluorides are heated in an atmosphere of PF_5, the alkali metal hexafluorophosphates are formed. This indicates that at high temperatures there is an equilibrium, as shown below:

$$MPF_6 \rightleftharpoons MF + PF_5 \uparrow \qquad (13\text{-}6)$$

An interesting reaction of the diazonium salt is the thermal decomposition at relatively low temperatures to give phosphorus pentafluoride. This reaction offers a very convenient method for obtaining phosphorus pentafluoride in the laboratory, since the diazonium salt can be obtained commercially.[20] The equation for the decomposition of phenyldiazonium hexafluorophosphate is given below.

$$[(C_6H_5)N_2]^+[PF_6]^- \longrightarrow C_6H_5F + N_2\uparrow + PF_5\uparrow \qquad (13\text{-}7)$$

The alkali metal hexafluorophosphates form neutral aqueous solutions. These solutions are very stable with respect to hydrolysis in neutral or alkaline media. However, the hydrolysis proceeds at a reasonable rate in acidic solutions. The stability of the hexafluorophosphate ion in alkaline media is evidenced by the fact that it withstands the action of melted hydrates of alkali metal hydroxides and is split by anhydrous molten hydroxides only at temperatures above several hundred degrees.

No esters of the hexafluorophosphate anion are known, nor would they be expected. It is interesting to note that the PF_6^- ion does not exhibit appreciable toxicity, in spite of the fact that it has a very high fluorine content. Neither bacteria nor yeasts are affected by the presence of ammonium or potassium hexafluorophosphates in a concentration of 1% in their nutrient media.[3] Protozoa also are not hampered in their development Apparently the only harmful effects of alkali metal hexafluorophosphates on mammals are attributable to the hydrolysis observed in acid media.

Preparation and Properties of Difluorophosphates

The first preparation of difluorophosphate was obtained by reacting a mixture of ammonium fluoride and phosphorus pentoxide. From this reaction ammonium salts of both mono- and difluorophosphates are obtained.[21] These can be separated by extraction with alcohol and fractional crystallization. Details of the preparation of ammonium monofluorophosphate and difluorophosphate are given in *Inorganic Syntheses*.[22] The difluorophosphate anion, like the hexafluorophosphate anion, is readily precipitated as a nitron salt. Alkali metal salts can be made from the nitron salt by adding an alkali metal nitrate to a slurry of the latter to precipitate the highly insoluble nitron nitrate and leave the alkali metal difluorophos-

[20] Manufactured by the Ozark-Mahoning Co., Tulsa, Okla.

[21] J. M. G. Marquina, *Anales soc. españ. fis. y quím.*, **31**, 516 (1933); W. Lange, *Ber.*, **60B**, 962 (1927); *ibid.*, **62B**, 786 (1929).

[22] W. Lange, *Inorganic Syntheses*, McGraw-Hill Book Co., New York, 1946, Vol. II, pp. 155–58.

phate in solution. The alkali metal salt is then obtained by filtering off the insoluble nitron nitrate and evaporating the filtrate.

An interesting preparation of difluorophosphates from hexafluorophosphates has been given in the patent literature.[23] According to this technique, the difluorophosphate is obtained by combining the hexafluorophosphate with a sodium metaphosphate, as shown by the first equation below, or with an oxygen-containing compound that will give a volatile fluoride, as shown by the second equation below.

$$NaPF_6 + 2\ NaPO_3 \xrightarrow{\Delta} 3\ NaO_2PF_2$$

$$3\ KPF_6 + 2\ B_2O_3 \xrightarrow{\Delta} 4\ BF_3\uparrow + 3\ KO_2PF_2 \qquad (13\text{-}8)$$

Pure difluorophosphoric acid can be made[24] in appreciable quantities by reacting anhydrous monofluorophosphoric acid with gaseous phosphoryl fluoride according to the following equation.

$$H_2O_3PF + OPF_3 \longrightarrow 2\ HO_2PF_2 \qquad (13\text{-}9)$$

By means of this reaction, which takes place slowly, the problem of equilibrium reactions such as shown in equation 13-2 were avoided. The product is purified by distillation under reduced pressure. Anhydrous difluorophosphoric acid is produced on a small commercial scale by reacting phosphorus pentoxide with anhydrous hydrogen fluoride.[25] A mixture of acids, practically a mole-to-mole mixture of monofluoro- and difluorophosphoric acid, is obtained. With respect to corrosion, it is found that silver is better than aluminum and that stainless steel is satisfactory, although, if difluorophosphoric acid remains for several days in contact with stainless steel, it will usually become discolored through dissolution of certain components of the alloy. The difluorophosphoric acid is isolated in pure form by vacuum distillation. Obviously, the salts of difluorophosphoric acid can be made directly from the acid when precautions are taken to avoid hydrolysis of the acid.

As shown in Figure 13-5, the nuclear magnetic resonance spectrum of phosphorus in difluorophosphoric acid shows three peaks due to indirect spin-spin coupling between the two fluorine atoms and the phosphorus atom. As expected for a structure in which the two fluorines are covalently bonded to the phosphorus, the relative heights of the peaks are in the order of 1-2-1. The fluorine spectrum shows, at low resolution, a 1-1 doublet due

[23] H. Jonas, Ger. Pat. 813,848 (1951, assigned to Farbenfabriken Bayer).

[24] W. Lange and R. Livingston, *J. Am. Chem. Soc.*, **72**, 1280 (1950).

[25] L. C. Mosier and W. E. White, *Ind. Eng. Chem.*, **43**, 246 (1951).

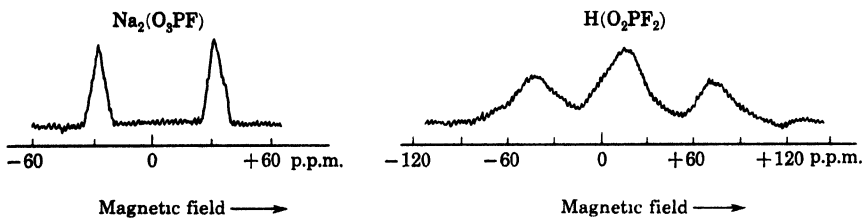
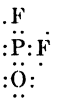


Fig. 13-5. Nuclear magnetic resonance of phosphorus in sodium monofluorophosphate and difluorophosphoric acid solutions The applied magnetic field was 9400 gauss, and the scale in the figures is parts per million of this field with respect to the resonance of orthophosphoric acid at 0 p.p.m.

to the spin-spin coupling with the phosphorus Obviously, the difluorophosphate anion exhibits the following structure in which two of the oxygen atoms in the tetrahedral orthophosphate anion are substituted by fluorine atoms. In this structure, the π-bonding is not shown



(13-10)

Anhydrous difluorophosphoric acid is a thin, clear liquid which forms dense, very irritating fumes on exposure to moist air. The acid has a melting point of $-96.5° \pm 1°$C. and a density (d_4^{25}) of 1.583. Its vapor pressure equation is given below, from which the heat of vaporization of 7.93 kcal./mole is calculated. The extrapolated boiling point at 760 mm. of Hg is 116°C.

$$\log p_{mm} = -1732\,2/T + 7\,332 \qquad (13\text{-}11)$$

A freshly made solution of difluorophosphoric acid behaves as a strong monobasic acid with a neutralization end point at about 7.3. Neutralized solutions become acidic at a moderate rate, due to hydrolysis to monofluorophosphate and fluoride anions.

Generally speaking, difluorophosphates of limited solubility correspond to perchlorates of limited solubility, although the known difluorophosphates show, without exception, a greater solubility in water than do the perchlorates. Relatively insoluble difluorophosphates are obtained with the tetramethylammonium ion and with the alkaloids: strychnine, brucine, morphine, and cocaine. The nitron salt, $C_{20}H_{16}N_4 \cdot HO_2PF_2$, which is used for analytical purposes, exhibits a solubility of 1:300 in water at 18°C. and has an uncorrected melting point of 230.5–232.5°C Ammonium, sodium, po-

tassium, and cesium difluorophosphates are all very soluble in water. The ammonium salt, which is extremely soluble, has a melting point of 213°C. As previously mentioned under the acid, the difluorophosphate anion is the most unstable of the fluorophosphate anions with respect to hydrolysis. Not only does it hydrolyze rapidly in hot acidic and basic media, but it is only moderately stable in hot neutral solution. Even at low temperatures near 0°C., solutions of the alkali metal difluorophosphates become acidic upon prolonged storage. Esters of difluorophosphoric acid are known and will be discussed in a following section entitled Halophosphate Esters.

Preparation and Properties of Monofluorophosphates

Probably the best preparative method for making alkali metal monofluorophosphates is to fuse a mixture of the alkali metal metaphosphate with the alkali metal fluoride in a closed vessel from which moist air is excluded. This technique has been described in some detail for sodium monofluorophosphate,[26] the equation for the formation of which is given below.

$$NaPO_3 + NaF \rightarrow Na_2O_3PF \qquad (13\text{-}12)$$

Details for the preparation of silver monofluorophosphate are also given.[26] Anhydrous monofluorophosphoric acid is made by a similar procedure in which a phosphoric acid of the metaphosphate composition is reacted with hydrofluoric acid.[27] In both cases, a reasonably pure product is formed.

Most of the discussion of monofluorophosphates in the literature covers compounds prepared by either precipitating from aqueous solutions of the ammonium salt,[21,22] fractionating from the difluorophosphate, or by reaction of a halide with the well-crystallized silver monofluorophosphate.[3] As shown in Table 13-2, silver monofluorophosphate is quite insoluble, whereas silver difluorophosphate, like silver perchlorate, is reasonably soluble, so that silver ion can be used to precipitate the monofluorophosphate ion from a solution containing monofluoro- and difluorophosphates.

As shown in Figure 13-5, the nuclear magnetic resonance spectrum of phosphorus in the monofluorophosphate anion exhibits a 1-1 doublet, which would be expected for a single fluorine atom covalently bonded to the phosphorus. Likewise, the fluorine atoms also exhibit a 1-1 doublet, due to indirect spin-spin splitting by the phosphorus. This means that the mono-

[26] O. F. Hill and L. F. Audrieth, *Inorganic Syntheses*, ed. L. F. Audrieth, McGraw-Hill Book Co., New York, 1950, Vol. III, pp. 106–09; C. O. Anderson, U. S. Pat. 2,481,-807 (1949, assigned to Ozark-Mahoning Co.).

[27] W. Lange and R. Livingston, *J. Am. Chem. Soc*, **69**, 1073 (1947).

fluorophosphate anion consists of a tetrahedral orthophosphate group in which one of the oxygens has been substituted by a fluorine atom.

A pH titration curve for sodium monofluorophosphate is shown in Figure 13-6. The ionization constants of monofluorophosphoric acid have been estimated in an approximate manner from these curves.[28] The values are $K_1 = 0.28$ and $K_2 = 1.58 \times 10^{-5}$.

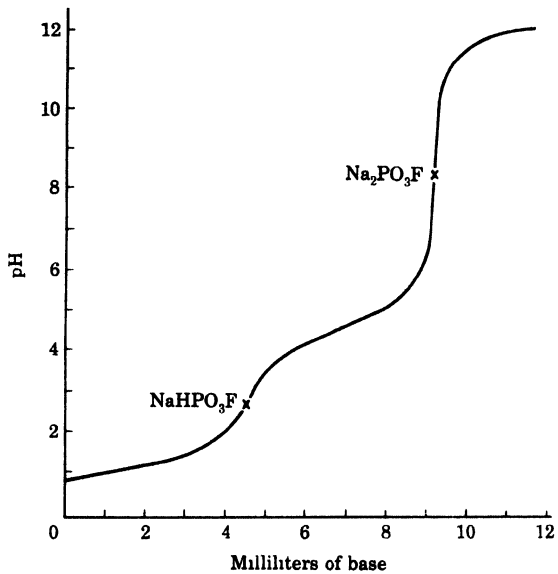


Fig. 13-6. Titration of monofluorophosphoric acid. The first end point at pH 2.8 corresponds to one equivalent of base per atomic weight of phosphorus

The solubilities of various monofluorophosphate salts are quite similar to those of the sulfates. This is illustrated for a number of slightly soluble salts in Table 13-2. The similarity between the monofluorophosphates and the sulfates is close, and that some monofluorophosphates are isomorphous with the corresponding sulfates. There are a number of papers in the literature in which this isomorphism is discussed.[29] It is interesting to note that there are some monofluorophosphates which are isomorphous with alum. These are $(NH_4)_2O_3PF \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$ and $(NH_4)_2O_3PF \cdot Al_2$-

[28] L. V. Devonshire, Ph.D. Thesis, University of Oklahoma, Norman, Okla., 1954.

[29] H. C. Goswami, *J. Indian Chem. Soc.*, **14**, 660 (1937); P. C. Ray, *Nature*, **126**, 310 (1930); W. Lange, *ibid.*, **126**, 916 (1930); *Ber.*, **62B**, 793 (1929); also see E. Bengtsson, *Arkiv Kemi, Mineral. Geol.*, **15B**, No. 7, 1 (1941).

TABLE 13-2
Solubilities of Some Monofluorophosphates and Sulfates in Water at Room Temperature (20°C.)

Salt	Solubilities in moles/l.	
	Monofluoro-phosphates	Sulfates
Normal calcium, dihydrate	6.3×10^{-2}	1.5×10^{-2}
Normal strontium, monohydrate	5.5×10^{-2}	6×10^{-4}
Normal barium	6×10^{-4}	1×10^{-5}
Silver	5.93×10^{-2}	2.51×10^{-2}
Normal lead	3.2×10^{-4}	1.3×10^{-4}
Mercurous	5×10^{-4}	8×10^{-4}

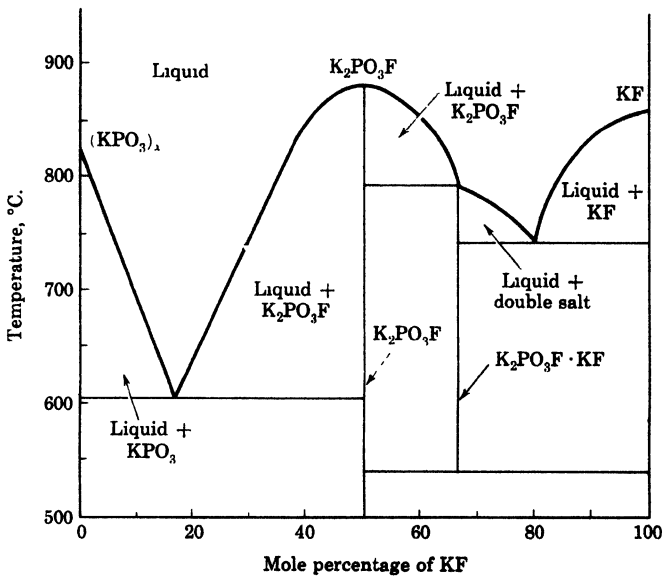


Fig. 13-7. The phase diagram for the system KPO_3–KF.

$(O_3PF)_3 \cdot 24\ H_2O$. Other double salts for which there are well-known sulfate analogs have also been described for the monofluorophosphates. The solubility of sodium[6] and calcium monofluorophosphates,[30] Na_2O_3PF and $CaO_3PF \cdot 2\ H_2O$, are shown in Figure 13-4.

As previously noted (see equation 13-12), alkali metal metaphosphates

[30] H. H. Rowley and J. E. Stuckey, *J. Am. Chem. Soc.*, **78**, 4262 (1956).

react with alkali metal fluorides to give the respective monofluorophosphates. The phase diagram between potassium metaphosphate (Kurrol's salt) and potassium fluoride was worked out a number of years before the discovery of the fluorophosphates,[31] and a maximum in the melting point curve was found at the composition corresponding to potassium monofluorophosphate as shown in Figure 13-7. Apparently there is a double salt between potassium monofluorophosphate and potassium fluoride exhibiting an incongruent melting point. The crystalline ammonium salt, $(NH_4)_2O_3PF \cdot H_2O$, loses its water of crystallization on heating at 105°C. At higher temperatures, it also loses one molecule of ammonia to give an acid

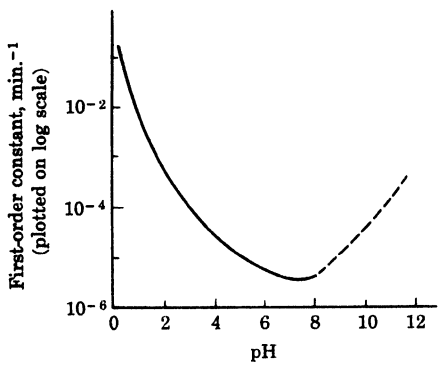


Fig. 13-8 Variation of the rate of hydrolysis of the monofluorophosphate anion as a function of pH at 80°C.

salt, NH_4HO_3PF, which melts without decomposition at 225.5°C. The sodium salt, Na_2O_3PF, melts at about 625°C. It is believed to form a hydrate when crystallized from very cold aqueous solution.

Monofluorophosphoric acid is an oily liquid which, to date, has not been distilled. It exhibits good thermal stability, has practically no odor, and in the absence of moisture does not attack glass. Upon cooling, it sets to a rigid glass at dry-ice temperatures. The density of the 100% acid is 1.818. The viscosity of the concentrated acid is approximately that of concentrated sulfuric acid, which it resembles to a considerable extent. Monofluorophosphoric acid has one strongly acid hydrogen, whereas the second hydrogen is much weaker. The titration curve of monofluorophos-

[31] M. Amadori, *Atti accad. nazl Lincei, Mem. Classe. sci fis. mat. e nat.. Sez II*, **21**, 688 (1913).

phoric acid is very similar to that of orthophosphoric acid, in which the third hydrogen is so weak that it hardly affects the basic region of the titration curve.

In neutral or weakly alkaline media, the monofluorophosphate anion is quite stable with respect to hydrolysis,[28] as shown by Figure 13-8. The activation energy for hydrolysis is about 8 kcal./mole.[28] Heating in strongly alkaline or strongly acidic solution results in rapid hydrolysis.

Not only does hydrolysis happen rapidly in hot dilute acid to form the orthophosphate ion and the fluoride ion, but, in concentrated solutions of the acid, the equilibrium shown in equation 13-2 is set up. Lange has studied[32] the hydrolysis equilibrium corresponding to the first step shown in equation 13-2, which is reproduced below in expanded form:

$$H_2O_3PF + H_2O = HF + H_3PO_4 \qquad (13\text{-}13)$$

When an equilibrium constant equal to $[H_2O_3PF][H_2O]/[H_3PO_4][HF]$ is set up on a mole fraction basis, it is found to vary from 0.31 at large concentrations of water to about 0.8 at low concentrations of water, going through a maximum of about 3.5 in between. Addition of strong acids causes an increase in the value of this equilibrium "constant." For example, addition of 70% perchloric acid can drive the value up to 23.7. Although the effect of added strong acids is qualitatively in accord with the idea of suppressing the electrolytic dissociation of orthophosphoric acid, it was also necessary for Lange to postulate the binding of water by this acid in order to explain quantitatively the results obtained with different strong acids. The whole subject of equilibria between the different fluorophosphoric acids, hydrogen fluoride, and water should be reinvestigated, using up-to-date physical tools, such as nuclear magnetic resonance, for chemical analysis.

Organic Halophosphates and Related Compounds[34]

By reacting alcohols with phosphorus trihalides or with phosphorus oxyhalides, a rather extensive series of halophosphite and halophosphate esters can be formed, where the halogen is bromine, chlorine, or fluorine. The existence of the esters of extremely unstable acids such as monochloro- or dichlorophosphoric acid is not surprising, since the preparation of these esters is carried out in nonaqueous systems in which there is no chance for the free acid to form. Typical reactions involved in the preparation of halophosphites are given in condensed form on the next page:

[32] W. Lange, *Ber.*, **62B**, 1084 (1929); *Z. anorg. u. allgem Chem.*, **214**, 44 (1933).

$$ROH + PX_3 \longrightarrow (RO)PX_2 + HX \uparrow$$
$$2\,ROH + PX_3 \longrightarrow (RO)_2PX + 2\,HX \uparrow \qquad (13\text{-}14)$$

In any case, the yield from the reaction shown by either of these equations is low. Indeed, it has been generalized[33] that primary aliphatic alcohols yield dichlorophosphites, secondary alcohols yield primary olefins, and tertiary alcohols yield alkyl chlorides when mixed with a slight excess (above a 1:1 mole ratio) of phosphorus trichloride. However, this rule does not always hold.[34] In the aromatic series of primary alcohols, the first equation shown in 13-14 usually proceeds without many complications. This is also true to a lesser extent for the second equation. In the second equation the aliphatic alcohols give very poor yields of monochlorophosphites, with the exception of glycols from which cyclic monochlorophosphites are obtained in fair yields. Thus, for ethylene glycol, we have the following equation.[35]

$$HOCH_2CH_2OH + PCl_3 \longrightarrow \begin{matrix} CH_2{-}O \\ | \quad\quad \diagdown \\ CH_2{-}O \end{matrix} P{-}Cl + 2\,HCl \qquad (13\text{-}15)$$

In this reaction a small amount of water apparently plays the role of a catalyst. It should be noted that dialkyl chlorophosphites have often been prepared by using the sodium alcoholate instead of the alcohol in equation 13-14.

An interesting reaction between phosphorus trihalides and cyclic organic oxides, imines, and sulfides has been described.[36] The reaction, which is shown below for ethylene oxide, is carried out simply by passage of the gaseous oxide into the phosphorus trichloride or tribromide until the required gain in weight is achieved. Good cooling is needed, since the reaction is highly exothermic and the temperature must be kept relatively low (15–20°C. for PCl_3 and −10 to 0°C. for PBr_3) in order to avoid side reactions.

$$\begin{matrix} CH_2{-}CH_2 \\ \diagdown\,\diagup \\ O \end{matrix} + PCl_3 \longrightarrow ClCH_2CH_2OPCl_2$$

$$\begin{matrix} CH_2{-}CH_2 \\ \diagdown\,\diagup \\ O \end{matrix} + ClCH_2CH_2OPCl_2 \longrightarrow (ClCH_2CH_2O)_2PCl \qquad (13\text{-}16)$$

[33] Ya. Yaroshenko, *J. Russ. Phys.-Chem. Soc.*, **29**, 223 (1897).

[34] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, 1950.

[35] A. E. Arbusov, V. M. Zoroastrova, and N. I. Rizpolozhenskii, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, **1948**, 208.

[36] M. I. Kabachnik, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **1947**, 631; M. I. Kabachnik and P. A. Rossiiskaya, *ibid.*, **1946**, 295, 403, 515; *ibid.*, **1948**, 95.

A number of dihalophosphites in which the halogen is either chlorine or bromine have been described.[34] In addition, some thio derivatives, *e.g.*, $(C_5H_5S)PCl_2$, are known. These compounds form complexes with such salts as the cuprous halides—compounds in which phosphorus donates its unshared pair of electrons to the metal atom. Nearly all of the monohalophosphites described in the literature are derivatives of chlorine. Both aromatic and aliphatic derivatives are known, as well as one thio compound, $(C_2H_5S)_2PCl$.

The simplest and most commonly used method for the preparation of halophosphates consists of reacting the proper alcohol or phenol with a phosphoryl halide or a thiophosphoryl halide.[34] The ratio of monohalo- to dihalophosphate produced in the reaction depends on the relative proportions of the reagents used, as roughly indicated by the following idealized equations

$$\begin{aligned} &ROH + OPX_3 \longrightarrow HX + (RO)P(O)X_2 \\ &2\ ROH + OPX_3 \longrightarrow 2\ HX + (RO)_2P(O)X \end{aligned} \qquad (13\text{-}17)$$

Removal of the hydrogen halide is usually accomplished by carrying out the reaction under reduced pressure with agitation or by bubbling an inert gas, such as nitrogen, through the reaction mixture.

The use of phosphorus oxyfluorodichloride in the reaction with alcohols results[3,37] in substitution of the two chlorine atoms to yield dialkyl fluorophosphates, when the reaction is run in the cold.

$$OPCl_2F + 2\ ROH \longrightarrow 2\ HCl\uparrow + (RO)_2P(O)F \qquad (13\text{-}18)$$

This reaction is an interesting example of the use of positional synthesis methods in phosphorus chemistry. In this case the more labile P—Cl bond is attacked in preference to the P—F bond.

Esters of the fluorophosphoric acids have also been prepared by exchange of halogen between sodium fluoride and the respective chlorophosphate ester. Another interesting preparation of the monoester of monofluorophosphoric acid is the reaction between the diester of pyrophosphoric acid and anhydrous hydrogen fluoride which gives a mixture consisting predominantly of the monoalkyl orthophosphate and monoalkyl monofluorophosphate.[38]

The dialkyl monofluorophosphate esters are extremely toxic, acting to inhibit cholinesterase. Because of this, these compounds were extensively studied as war gases.[3,39] A discussion of the structural requirements for

[37] N. B. Chapman and B. C. Saunders, *J. Chem. Soc.*, **1948**, 1010.

[38] A. Hood and W. Lange, *J. Am. Chem. Soc.*, **72**, 4956 (1950).

[39] M. F. Sartori, *Chem. Revs.*, **48**, 225 (1951).

high toxicity and miotic action of the esters of fluorophosphate esters has been given in the literature.[40] It is interesting to note that the monoalkyl monofluorophosphates do not have the typical toxic properties exhibited by the dialkyl esters.[3] The toxicology of these compounds is discussed in Volume II of this work.

An interesting reaction for the preparation of halothionophosphates is the reaction between the halophosphites and elementary sulfur, which may be carried out in boiling carbon disulfide in the case of the alkyl dichlorophosphites but must be done at higher temperatures for the aryl derivatives. Similar derivatives can be made by using selenium instead of sulfur.

$$(RO)PX_2 + S \longrightarrow (RO)P(S)X_2$$

$$(RO)_2PX + S \longrightarrow (RO)_2P(S)X \qquad (13\text{-}19)$$

By using mercaptans with phosphoryl chloride or thiophosphoryl chloride, thio derivatives of the halophosphates have been made with all of the possible combinations of sulfur atoms substituting for from one to all of the oxygen atoms.

An interesting reaction between phosphorus pentachloride and hydroxybenzoic or hydroxyarylsulfonic acids has been studied.[34] The reaction is shown below in idealized form.

$$C_6H_4(OH)COOH + PCl_5 \longrightarrow C_6H_4(COCl)OP(O)Cl_2 + 2\ HCl\uparrow \qquad (13\text{-}20)$$

In Table 13-3 the properties of some typical halophosphite and halophosphate esters are presented. The kinetics of the hydrolysis of diisopropyl fluorophosphate has been carefully investigated,[41] and a mechanism for the process has been proposed. Both acids and bases catalyze the hydrolysis whereby the fluorine atom is substituted by an hydroxyl group. It should be noted that this hydrolytic reaction is much faster than the one in which an isopropyl group is removed from the molecule to give isopropyl alcohol and the monoester. The activation energy for the process whereby F is replaced by —OH is found to be 13.5 kcal./mole. In order to explain the data, it was necessary to assume two separate and distinct activated complexes in the rate process—one for the acid-catalyzed and one for the base-catalyzed reaction. Enzymes greatly accelerate[42] the scission of the P—F bond and the C—O—P linkages in the dialkyl fluorophosphates.

[40] H. G. Cook, B. C. Saunders, and F. E. Smith, *J. Chem. Soc.*, **1949**, 635; also see B. C. Saunders, G. J. Steacy, F. Wild, and I. G. E. Wilding, *ibid.*, **1948**, 699.

[41] M. Kilpatrick and M. L. Kilpatrick, *J. Phys. & Colloid Chem.*, **53**, 1371, 1385 (1949); W. A. Waters and C. G. de Worms, *J. Chem. Soc.*, **152**, 926 (1949).

[42] L. A. Mountier and L. T. H. Dien, *Proc. Soc. Exptl. Biol. Med.*, **87**, 40 (1954).

TABLE 13-3
Examples of Organic Halophosphites and Halophosphates

Compound	Properties
$(CH_3O)PCl_2$	b.p. = 96°C.; d_4^{20} = 1.3980
$(C_6H_5O)PCl_2$	b.p.$_{11mm}$ = 90°C.; d_4^{20} = 1.3543
$(C_6H_5O)PBr_2$	b..p$_{11mm}$ = 130–132°C.
$(C_6H_5O)_2PCl$	b.p.$_{11mm}$ = 172°C.; d_{18}^{18} = 1.221
$(C_6H_5O)_2PBr$	b p.$_{11mm}$ = 189–92°C.
	b.p.$_{16mm}$ = 41 5°C.; d_4^{20} = 1 4199
$(C_2H_5O)P(O)F_2$	b.p.$_{760mm}$ = 85–86°C.
$(C_2H_5O)P(S)F_2$	b.p.$_{760mm}$ = 78.4°C.; m.p. = −124°C.
$(C_2H_5O)P(O)Cl_2$	b.p.$_{20mm}$ = 65°C.; d_4^{19} = 1 353
$(C_2H_5O)P(S)Cl_2$	b p.$_{20mm}$ = 52°C.
$(C_2H_5S)P(S)Cl_2$	b.p.$_{10mm}$ = 92°C.
$(C_2H_5O)_2P(O)F$	b.p.$_{10mm}$ = 60°C.
$(C_2H_5O)_2P(O)Cl$	b.p.$_{10mm}$ = 93–94°C.
$(C_2H_5O)_2P(S)Cl$	b.p.$_{10mm}$. = 85°C.; b.p.$_{2mm}$. = 60°C.
$(C_6H_5O)P(O)Cl_2$	b p.$_{16mm}$ = 128°C.
$(C_6H_5O)P(S)Cl_2$	b p $_{16mm}$ = 132°C.
$(C_6H_5S)P(S)Cl_2$	b.p.$_{16mm}$ = 168–70°C.
$(C_6H_5O)_2P(O)Cl$	b.p.$_{760mm}$ = 314–316°C.; b.p.$_{11mm}$. = 193°C
$(C_6H_5O)_2P(S)Cl$	b.p $_{11mm}$ = 200°C.; m.p. = 72 5°C
$(C_6H_5O)_2P(Se)Cl$	m.p. = 64–65°C.

PEROXYACIDS OF PHOSPHORUS

Perphosphoric Acids and Their Salts

Generally speaking, the methods which have been used successfully for the preparation of persulfuric acid and the persulfates have also been applied to perphosphoric acid and the perphosphates. These procedures consist of anodic oxidation and reaction of the anhydride with hydrogen peroxide.

Alkali metal and ammonium salts of the perphosphates have been prepared by electrolytic oxidation.[43,44] As in the formation of persulfates, low temperatures are advantageous, and the presence of small amounts of fluorides and chromates increases the yield of the peroxyacids, probably by maintaining a high anodic over-voltage. Low current densities, about 0.15 amp./cm.^{2} or less, at the anode are favorable. Electrolysis of a solution containing dipotassium phosphate plus potassium fluoride gives a mixture of $K_4P_2O_8$ and K_2HPO_5. Alkalinity favors the formation of the $P_2O_8^{4-}$ an-

[43] F. R. Fichter and E. Gutzwiller, *Helv. Chim. Acta*, **11**, 323 (1928); F. R. Fichter and A. Rius y Miro, *ibid.*, **2**, 3 (1919); A. Rius y Miro, *Anales fis. y quim.*, **16**, 573 (1918); also see F. R. Fichter and K. Kestenholz, *Helv. Chim. Acta*, **23**, 209 (1940).

[44] S. Husain and J. R. Partington, *Trans. Faraday Soc.*, **24**, 235 (1928).

ion; whereas the PO_5^{3-} anion is produced in larger yield in acid solution. By choosing proper conditions, it is possible to obtain an 80% yield of $K_4P_2O_8$, which can be crystallized.

Mixing solutions of this perdiphosphate with soluble salts of barium, zirconium, or lead gives the respective sparingly soluble perdiphosphates: $Ba_2P_2O_8$, $Zn_2P_2O_8$, and $Pb_2P_2O_8$. The silver salt, $Ag_4P_2O_8$, is obtained as a colorless precipitate when silver nitrate and potassium perdiphosphate are brought together at $-15°C.$ in a saturated solution of ammonium nitrate.[45] The precipitate quickly decomposes and becomes dark brown on standing. Likewise, the potassium permonophosphate gives, with silver nitrate, a dark precipitate which changes to white Ag_3PO_5 and then to yellow Ag_3PO_4 with evolution of ozone and oxygen.

Perphosphates of rubidium and cesium are more easily prepared than those of potassium, even in the absence of fluorides or chromates; however, rather higher current densities are required in their preparation.[44] Although ammonium perphosphates can be prepared in good yield by electrolysis, an autoredox reaction may occur to give ammonium orthophosphate and ammonium nitrate.

Although hydrogen peroxide does not combine with orthophosphoric acid to give perphosphates, a 30% solution of H_2O_2 at 0°C. will react with phosphorus pentoxide or an ultraphosphate to give permonophosphoric acid.[46] This reaction is readily carried out by suspending the phosphorus pentoxide in acetonitrile, a solvent in which permonophosphoric acid is quite stable. It is interesting to note that bubbling[47] elemental fluorine through phosphoric acid in the cold also leads to a mixture of H_3PO_5 and $H_4P_2O_8$. The best yield is obtained from a relatively concentrated solution containing about 5 moles/l. of H_3PO_4. Provided that the solution is kept slightly alkaline, alkali metal phosphates yield salts of perdiphosphoric acid, $H_4P_2O_8$, under the same conditions, whereas sodium and potassium pyrophosphates give the corresponding permonophosphates.

Although their structures have not been proven definitely, it is believed that the two perphosphate anions can be formulated as follows. The formulation of the perdiphosphate anion is assumed by analogy to the perdisulfate anion, the structure of which is derived from an x-ray study[48] of its ammonium and cesium salts.

[45] F. R. Fichter and C. Simon, *Helv. Chim. Acta*, **13**, 398 (1930).

[46] G. Toennies, *J. Am. Chem. Soc.*, **59**, 555 (1937); J. Schmidlin and P. Massini, *Ber.*, **43**, 1162 (1910); J. d'Ans, *Z. Electrochem.*, **17**, 850 (1911). J. d'Ans and W. Friederich, *Ber.*, **43**, 1880 (1910); *Z. anorg. Chem.*, **73**, 343 (1911).

[47] F. Fichter and H. Wolfmann, *Helv. Chim. Acta*, **9**, 559 (1927).

[48] R. C. L. Mooney and W. H. Zachariasen, *Phys. Rev.*, **44**, 327 (1933).

permonophosphate perdiphosphate (13-21)

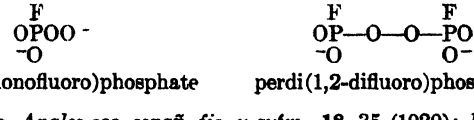
Permonophosphoric acid is a strong oxidizing agent. It liberates iodine at once from acidified potassium iodide and oxidizes manganous salts to permanganates in the cold. It undergoes hydrolysis in dilute solution to give orthophosphoric acid and hydrogen peroxide. This reaction is apparently autocatalytic, since H_3PO_5 reacts with hydrogen peroxide to give orthophosphoric acid plus oxygen gas [49] Perdiphosphoric acid liberates iodine much more slowly from acidified potassium iodide and can be kept for relatively long periods of time in dilute solution. Oxidation of manganous salts in acid solution to red manganic salts is characteristic of true perphosphates as compared to peroxyhydrates. The perphosphoric acids exhibit this reaction. An interesting application for perphosphoric acid is the detoxification of hydrogenation catalysts which have been poisoned by small concentrations of carbon disulfide or other sulfides.[49]

Other Peroxyacids of Phosphorus

When sodium hypophosphite is oxidized in dilute solution by oxygen containing a small amount of ozone or fluorine, permonophosphorous acid is formed.[50] Presumably, the anion of this acid has the following structure.

 (13-22)

Two perfluorophosphoric acids are said to have been obtained by anodic oxidation of monofluorophosphoric acid or the sodium, potassium, or ammonium monofluorophosphates.[51] Although these peracids or their salts have not been isolated, their composition has been calculated from analysis of the electrolyte, and their structures are assumed to have the following forms, by analogy with the two perphosphoric acids.



permono(monofluoro)phosphate perdi(1,2-difluoro)phosphate (13-23)

[49] A. Rius y Miro, *Anales soc. españ. fis. y quím.*, **18**, 35 (1920); *Helv. Chim. Acta*, **3**, 347 (1920); E. B. Maxted and A. Marsden, *J. Chem. Soc.*, **1946**, 23.

[50] W. Bockemüller and T. Götz, *Ann.*, **508**, 263 (1934).

[51] J. M. G. Marquina, *Rev. acad. cienc. Madrid*, **30**, 382 (1933); *Anales soc. españ. fis. y quím.*, **31**, 840 (1933).

Peroxyhydrates of Phosphates

Alkaline or neutral ortho-, pyro-, tripoly-, or trimetaphosphates form[44,52] a number of compounds with hydrogen peroxide in which the H_2O_2 molecule plays about the same role as H_2O does in the hydrates. Examples of this type of compound for the orthophosphates are: $Na_3PO_4 \cdot 2\ H_2O_2$, $Na_2HPO_4 \cdot 2\ H_2O_2$, $KH_2PO_4 \cdot 1.25\ H_2O_2$, and $K_2HPO_4 \cdot 2.5\ H_2O_2$; for the pyrophosphates: $K_4P_2O_7 \cdot 3\ H_2O$ and $(NH_4)_2H_2P_2O_7 \cdot H_2O_2 \cdot 2\ H_2O$; for the tripolyphosphate: $Na_5P_3O_{10} \cdot 2\ H_2O_2 \cdot H_2O$; and for the trimetaphosphate: $Na_3P_3O_9 \cdot H_2O_2$. These compounds are all true peroxyhydrates which yield hydrogen peroxide immediately when in contact with water and do not oxidize iodine so rapidly as the salts of true peroxyacids. The peroxyhydrates are usually prepared by simply mixing a concentrated hydrogen peroxide—say, 60% H_2O_2—with the respective anhydrous salt.

THIO SALTS AND ESTERS

In the anions of all of the various oxyacids of phosphorus it is possible to substitute from one to all of the oxygen atoms by sulfur. The thio compounds thus obtained react more or less rapidly with water when in aqueous solution to give hydrogen sulfide by a process in which the sulfur is replaced by the oxygen of the water. Although there are not sufficient data on which to base a firm conclusion, it appears that the rate of this process is considerably faster the more sulfur atoms there are in the molecule-ion, especially when the several sulfur atoms are attached to the same phosphorus. In addition, it is well known that the rate of exchange of oxygen for sulfur is very fast in acidic aqueous solutions. This means that the thioacids are quite unstable *per se*, so that in most cases only their salts have been obtained.

Various Thio Salts

An interesting procedure for preparing thio salts of phosphorus-based acids is to heat stoichiometric mixtures of the respective elements together in sealed tubes.[2,53] By this procedure a number of crystalline substances corresponding to thiophosphites, M_3PS_3; a thiopyrophosphite,[2] $Ag_4P_2S_5$; thiohypophosphates, $M_4P_2S_6$; and thiopyrophosphates, $M_4P_2S_7$, have been

[52] H. Menzel and C. Gäbler, *Z. anorg. Chem.*, **177**, 187 (1929); P. Bonneman-Bémia, *Ann. chim.*, **16**, 395 (1941).

[53] L. Ferrand, *Ann. chim. et phys.*, **17**, 388 (1899); *Compt. rend.*, **122**, 621, 886 (1896); C. Friedel, *ibid.*, **119**, 260 (1894); *Bull. soc. chim.*, **11**, 115 (1894).

obtained. In a somewhat similar procedure,[54] metal sulfides are heated with phosphorus sulfides, or the vapors of phosphorus sulfides are passed over the metal halide. By this latter technique, a number of thio(ortho)-phosphates, M_3PS_4, were produced, as well as some thiopyrophosphates and a thiophosphite.

Normal and acid salts of thiophosphates and thiophosphites have also been made by reacting phosphorus sulfides with concentrated aqueous solutions of metal ions.[55–57] Thus, by dissolving P_4S_3 in alkalies there results a complicated reaction in which phosphine, hydrogen, and what is presumably red phosphorus are produced. By vacuum evaporation of the resulting filtered aqueous solution from the reaction between P_4S_3 and NaOH, crystals having a composition equivalent to $Na_2(HPO_2S)\cdot 2\ H_2O$ have been obtained. With an excess of sodium hydroxide, the "normal" salt, Na_3PO_2S, is said to be crystallized. By replacing the sodium hydroxide by sodium sulfide, the solution obtained from P_4S_3 gives a salt corresponding to $Na_2(HPOS_2)\cdot 2.5\ H_2O$.

Similarly, addition of P_4S_{10} to a saturated solution of sodium sulfide gives the completely sulfur-substituted orthophosphate $Na_3PS_4\cdot 8\ H_2O$. On the other hand, with a somewhat different treatment, the salt $Na_3POS_3\cdot 11\ H_2O$, can be prepared by reacting thiophosphoryl chloride with a solution of sodium hydroxide or by heating a solution prepared by dissolving phosphorus pentasulfide in sodium hydroxide, in order to decompose the higher thiophosphates. The chemistry of these reactions has recently been reviewed by Klement,[56] who also was able to isolate the monothio(ortho)- and dithio-(ortho)phosphoric acids. A number of insoluble salts such as the lead and silver salts can be made by metathesis in aqueous solution.

An interesting preparation of a thiopyrophosphate (Michaelis[55]) is the reaction of thiopyrophosphoryl tetrabromide, $Br_2(S)PSP(S)Br_2$, with water to give a number of products, including trithiopyrophosphoric acid, $H_4P_2O_4S_3$. From the reaction of dry hydrogen sulfide with ammonium trithiophosphate at 175°C., Stock[54] reported the formation of ammonium dithio-

[54] H. E. Wallsom, *Chem. News*, **136**, 113 (1928); A. Stock, *Ber.*, **39**, 1967 (1909); A. Stock and B. Hoffman, *ibid.*, **36**, 314 (1903); E. Gatzel, *Z. anorg. Chem.*, **4**, 186 (1893); *Ber.*, **24**, 3886 (1891); L. Ferrand, *Bull. soc. chim.*, **13**, 115 (1895); E. Baudrimont, *Compt. rend.*, **55**, 323 (1862).

[55] F. Ephraim and E. Majler, *Ber.*, **43**, 285 (1910); F. Ephraim and R. Stein, *ibid.*, **44**, 3409 (1911); E. Gatzel, *Z. anorg. u. allgem. Chem.*, **44**, 65 (1905); C. Kubierschky, *J. prakt. Chem.*, **31**, 93 (1885); G. Lemoine, *Compt. rend.*, **93**, 489 (1881); A. Michaelis, *Ann.*, **164**, 39 (1872).

[56] R. Klement, *Z. anorg. Chem.*, **253**, 237 (1947).

[57] P. Neogi and M. C. Ghosh, *J. Indian Chem. Soc.*, **6**, 599 (1929).

metaphosphate, $[(NH_4)PO_2]_n$, the anion of which is presumably a cyclic structure similar to the trimeta- and tetrametaphosphate anions.

An x-ray study has been carried out on cuprous thiophosphate,[58] Cu_3PS_4, which was prepared by simply heating together copper, red phosphorus, and sulfur. The crystals are rhombic, with two molecules in the elementary cell. The PS_4^{3-} ion, having a tetrahedral structure, is observed in the crystal which is isomorphous with the thioarsenate, Cu_3AsS_4.

The sorption of dithiophosphate on galena has been studied.[59] It is found that the interaction is not merely a matter of physical adsorption but appears to have characteristics of both chemisorption and chemical reaction at the surface.

Organic Derivatives of Various Thioacids of Phosphorus

Thio derivatives of all of the various oxyacids of phosphorus have been prepared. In these derivatives, the sulfur may play the role of a bridging atom between the phosphorus and the carbon of the organic radical, or it may be found in the isolated position, where it is bonded only to the phosphorus.

By warming primary phosphines with elemental sulfur, products are obtained which may be regarded as thiophosphinous acids with the empirical formula, $RPSH_2$. The only product in this category which has been satisfactorily characterized is the phenyl derivative,[60] $C_6H_5PSH_2$. In a similar manner, esters of phosphonous and phosphinous acids, as well as the corresponding thio derivatives, readily add sulfur upon heating,[34] as indicated by the following examples.

$$\begin{aligned} RP(OR')_2 + S &\longrightarrow RP(S)(OR)_2 \\ RP(SR')_2 + S &\longrightarrow RP(S)(SR')_2 \\ R_2P(SR') + S &\longrightarrow R_2P(S)(SR') \end{aligned} \qquad (13\text{-}24)$$

Another interesting reaction is the preparation of thioacids by combining Grignard reagents with phosphorus sulfides. Thus, by reacting an aliphatic Grignard with phosphorus pentasulfide, yields up to 50% of $H_2(RPOS_2)$ and up to 20% of $H(R_2PS_2)$ are obtained after careful hydrolysis of the reaction mixture obtained from refluxing in ether.

In Table 13-4, a listing is given of some typical thio derivatives of phosphorus-based acids containing C—P bonds and of the esters of various thio-

[58] A. Ferrari and L. Cavalca, *Gazz. chim. ital.*, **78**, 283 (1948).

[59] G. L. Simard, J. Chupak, and D. J. Salley, *Am. Inst. Mining Met. Engrs., Tech. Publ. No. 2815-B, Mining Eng.*, **187**, 359 (1950).

[60] H. Köhler, Ph.D. Thesis, Tubingen University, Germany, 1877, *Ber.*, **13**, 463 (1880).

acids of phosphorus. For details on the preparation of these compounds, the reader is referred to the text by Kosolapoff.[34]

TABLE 13-4
Effect of Substituting Sulfur for Oxygen in Organic Derivatives of Acids Based on Phosphorus

Compound	Properties
$(C_6H_5)_2P(OC_2H_5)$	b.p.$_{14mm}$ = 179°C.; d_0^0 = 1.0896
$(C_6H_5)_2P(SC_2H_5)$	b.p.$_{14mm}$ = 197–198°C.; d_0^0 = 1.133
$(C_6H_5)P(O)(OC_2H_5)_2$	b.p.$_{3.5mm}$ = 125°C
$(C_6H_5)P(S)(OC_2H_5)_2$	Undistillable oil; d_4^{15} = 1.12
$(C_6H_5)P(S)(SC_2H_5)_2$	b.p.$_{3.5mm}$ = 191–192°C d_4^0 = 1.220
$(C_3H_7O)_3P$	b.p.$_{15mm}$ = 91°C.; d_0^{22} = 0.950
$(C_3H_7S)_3P$	b.p.$_{15mm}$ = 164–169°C., d_4^{25} = 1.093
$(C_2H_5O)_3P$	b.p.$_{10mm}$ = 47°C.; d_0^{20} = 0.969
$(C_2H_5O)_2P(SC_2H_5)$	b.p.$_{10mm}$ = 75–77°C.; d_0^{20} = 1.021
$(C_2H_5O)P(SC_2H_5)_2$	b.p.$_{10mm}$ = 108–111°C., d_0^{20} = 1.068
$(C_2H_5S)_3P$	b.p.$_{10mm}$ = ca. 135°C.; d_0^{20} = 1.16
$(C_6H_5O)_2PO_2H$	m.p. = 61–62°C
$(C_6H_5O)_2PS_2H$	m.p. = 61°C.
$(C_2H_5O)_3PO$	b.p.$_{20mm}$ = 102°C., d_0^0 = 1.090
$(C_2H_5O)_2(C_2H_5S)PO$	b.p.$_{20mm}$ = 122°C.; d_0^0 = 1.125
$(C_2H_5O)(C_2H_5S)_2PO$	b.p.$_{20mm}$ = 148°C.; d_0^0 = 1.162
$(C_2H_5S)_3PO$	b.p.$_{20mm}$ = 175°C.; d_0^0 = 1.197
$(C_2H_5O)_3PS$	b.p.$_{20mm}$ = 106°C.; d_0^0 = 1.094
$(C_2H_5S)_3PS$	b.p.$_{20mm}$ = 182°C.; d_0^0 = 1.223

Because of the value of some of the esters of thiophosphoric acid as insecticides,[61] these esters have been rather extensively studied during the last decade. Thus, the rates of hydrolysis of ester groups from phosphates and thiophosphates have been compared.[62] As shown in Table 13-5, the rate of hydrolysis of the C—O—P linkage is considerably higher in the phosphates than in the corresponding thiophosphates. This is explained on the basis that the substitution of the isolated oxygen atom by the less electronegative sulfur causes the phosphorus to be less positive in the thiophosphate, so that the phosphorus is less able to contribute *d*-orbitals to the σ-bond base structure of an activated complex in which an oxygen atom from the water forms a fifth ligand attached to the phosphorus. The increase in rate of hydroly-

[61] R. L. Metcalf, *Organic Insecticides*, Interscience Publishers, New York, 1955, Chapt. XI, pp. 255–61.

[62] J. A. A. Ketelaar, H. R. Gersmann, and K. Koopmans, *Rec. trav. chim.*, **71**, 1253 (1952).

TABLE 13-5
Comparison of the Rate of Hydrolysis of Phosphate and Thiophosphate Esters in 50% Acetone Solution

Compound	Rate constant[a] at 25°C. (mole^{-1} min.$^{-1}$)	Activation energy[b] (kcal./mole)	Log frequency factor[b]
$OP(OC_2H_5)_2(OC_6H_4NO_2)$	0 40	12.4	8 64
$SP(OC_2H_5)_2(OC_6H_4NO_2)$	0 013	19 2	11.96
$OP(OC_2H_5)(OC_6H_4NO_2)_2$	31 5	14 3	11.96
$SP(OC_2H_5)(OC_6H_4NO_2)_2$	0 97	12 1	8 73
$OP(OCH_3)(OC_6H_4NO_2)_2$	34.3	13 4	11.25
$SP(OCH_3)(OC_6H_4NO_2)_2$	1 35	13 9	10 33
$OP(OC_6H_4NO_2)_3$	2060	4 10	6 34
$SP(OC_6H_4NO_2)_3$	12 4	5.70	5 21

[a] k = rate of formation of p-nitrophenol.

[b] The rate constant, k, is related to the frequency factor, f, and activation energy, E, by the equation: $k = fe^{E/RT}$ or $\log k = E/(2.30\,RT) + \log f$.

sis on adding more nitrophenyl groups to the compounds, as shown in Table 13-5, has a similar explanation since the strong electron-accepting tendency of the nitrophenyl group makes more probable the formation of the activated complex in which the phosphorus is assumed to be present as an sp^3d-hybrid. Superimposed on this explanation is the steric effect due to the large size of the nitrophenyl group. The low values of the frequency factor for the trinitrophenyl esters is probably attributable to this steric effect.

Optical resolution of an acid of phosphorus in which the optical activity is due to an asymmetric phosphorus atom has been achieved in the case of ethyl ethanethiophosphonic acid, $(C_2H_5O)(C_2H_5)POSH$, by fractional recrystallization of the quinine salt from an acetone-ether solvent.[63] The optical rotation constant is $(M)_D = -96.6$ for the dextro acid, the monohydrate of which melts at 151–153°C. with loss of the hydrate water.

In a recent note,[64] it was shown that the solubilities of thorium, uranyl, and cupric nitrates are more than 20 times greater in tri-*n*-butyl orthophosphate than in tri-*n*-butyl thioorthophosphate. This great difference in solubility indicates that the heavy metal ion is probably strongly coordinated by the unshared oxygen atom of the phosphate molecules of the solvent, whereas the unshared sulfur atom of the thiophosphate molecules has very little electron-donating ability. Other qualitative experiments described in the literature seem to bear out these conclusions.

[63] H. S. Aaron and J. I. Miller, *J. Am. Chem. Soc.*, **78**, 3538 (1956).

[64] W. W. Wendlandt and J. M. Bryant, *Science*, **123**, 1121 (1956).

The question of the existence of P—S bonds in the phosphates of biological systems has received considerable debate. For a while it was thought that in enzymatic acetylations coenzyme A reacts with adenosine triphosphate to give an orthophosphate or pyrophosphate derivative in which the coenzyme was bound to the ortho- or pyrophosphate moiety by a C—S—P linkage.[65] Later work has indicated that this is probably not the mechanism of acetylations and other biological processes involving the transfer of organic groups based on two carbon atoms. However, more recent data support the formation of orthophosphoryl-*S*-coenzyme A as an intermediate in succinate activation rather than in acetate activation.[66] Thus, it now seems that at least one thiophosphate is to be found as a naturally occurring biological compound. As would be expected, a number of thiophosphate derivatives of biologically active substances have been prepared *in vitro*.

Compounds with an —S—S— Linkage

Compounds with an —S—S— bridge have been prepared by oxidation of monothioorthophosphates, such as $Na_3PO_3S \cdot 12\ H_2O$, by iodine.[67] The salt $K_2[(HO)(O_2)PSSP(O_2)(OH)]$ forms good crystals which are relatively insoluble in water. Its saturated solution has a pH of 5. Barium ion does not give a precipitate with the $^{2-}O_3PSSPO_3^{2-}$ ion, but silver and lead ions do. In the presence of ammonium chloride and manganous chloride, the difficultly soluble salt, $Mn_3(OH)_2(O_3PSSPO_3) \cdot 3\ H_2O$, is formed. A material having the empirical formula $Mg_2P_2O_4S_4$ has been described.[67] If this represents a compound, it may have an —S—S— bridge between the two phosphorus atoms.

By the reduction of the salts of diesterified thiophosphates by iodine or bromine, it is possible to tie together two phosphorus atoms by an —S—S— bridge. This reaction and its thermodynamics have been studied in the case of esters in which the organic radicals ranged from methyl through amyl.[68] The reaction is carried out by suspending the diesterified salt in absolute ether and using an ethereal solution of bromine or iodine as the reducing agent. A typical ester, $(CH_3O)_2(O)PSSP(O)(OCH_3)_2$, is thus

[65] F. Lynen and E. Reichert, *Angew. Chem.*, **63**, 47 (1951); F. Lynen, E. Reichert, and L. Rueff, *Ann.*, **574**, 1 (1951); F. Lipmann, M. E. Jones, S. Black, and R. M. Flynn, *J. Am. Chem. Soc.*, **74**, 2384 (1952). For correction of this view, see M. E. Jones, F. Lipmann, H. Hilz, and F. Lynen, *J. Am. Chem. Soc.*, **75**, 3285 (1953). Also see S. Ochoa, *Advances in Enzymol.*, **15**, 250 (1954).

[66] R. A. Smith, I. F. Frank, and I. C. Gunsalus, *Federation Proc.*, **16**, 251 (1957).

[67] E. Thilo and E. Schöne, *Z. anorg. Chem.*, **259**, 225 (1949).

[68] O. Foss, *Acta. Chem. Scand.*, **1**, 8 (1947).

produced. This crystalline product, which melts at 31°C., is stable in dry air but reacts with moist air to precipitate sulfur. Degradation also occurs in contact with water, and it should be noted that the rate of degradation is unaffected by the pH of the water. Similar compounds also can be made with selenium in place of sulfur.[68] The redox reactions whereby the esters with —S—S— bridges are prepared represent equilibria as shown by the following equation.

$$2\ (RO)_2PSO^- + I_3^- \rightleftharpoons (RO)_2(O)PSSP(O)(OR)_2 + 3\ I^- \qquad (13\text{-}25)$$

It is found that the equilibrium constant for the above reaction increases considerably as the molecular weight of the alkyl group, R, is increased. Thus, for concentrations in moles per liter, the equilibrium constant is 0.2 for R = methyl, 3.6 for R = *n*-propyl, and 110 for R = isoamyl. Since the values of the equilibrium constants are quite dependent upon R, measurable equilibria are set up as follows.

$$(RO)_2(O)PSSP(O)(OR)_2 + 2\ (R'O)_2POS^- = 2\ (RO)_2POS^- + (R'O)_2(O)PSSP(O)(OR')_2 \qquad (13\text{-}26)$$

Similar equilibria can be measured in which one compound has a sulfur atom and the other a selenium atom, with the same or different alkyl radicals.

AMIDO- AND IMIDOACIDS, THEIR SALTS AND ESTERS

Both the monamido and diamido derivatives of the orthophosphate ion are known. They are the middle two members of the following series ranging from the orthophosphate ion to phosphoryl amide.

$$\left[\begin{matrix} O \\ OPO \\ O \end{matrix}\right]^{3-} \left[\begin{matrix} O \\ H_2NPO \\ O \end{matrix}\right]^{2-} \left[\begin{matrix} O \\ H_2NPNH_2 \\ O \end{matrix}\right]^{-} \quad \begin{matrix} O \\ H_2NPNH_2 \\ N \\ H_2 \end{matrix} \qquad (13\text{-}27)$$

According to recent American and British convention, the compound $H_2O_3P(NH_2)$ is known as phosphoramidic acid. However, throughout most of the literature, this compound is called monamidophosphoric acid. The derivatives are thus known as phosphoramidates or, by the earlier notation, monamidophosphates. In order to be precise, the prefix ortho should be used, *e.g.*, orthophosphoramidate or monamidoorthophosphate. Similarly, the acid $HO_2P(NH_2)_2$, is now known as phosphorodiamidic acid, although the name given to it in most of the literature is diamidophosphoric acid. Again, precise nomenclature demands the use of the prefix ortho, *e.g.*, orthophosphorodiamidate.

Orthophosphoramidites

By the action of ammonia on phosphorus trioxide, P_4O_6, dissolved in ether or benzene, a white solid was obtained[69] which was believed to have the formula $(NH_2)_2POH$ This material can be melted and sublimed with some decomposition and combines with water with such great violence that the mass becomes incandescent. Upon hydrolysis in hydrochloric acid, ammonium chloride and phosphorous acid are formed.

A number of organic substances have been prepared which can be considered as amido derivatives of phosphorous acid.[34] Thus, $(iso\text{-}C_4H_9)_2NP(OC_6H_5)_2$ has been made[70] by the following reaction.

$$(C_6H_5O)_2PCl + 2\ (iso\text{-}C_4H_9)_2NH \longrightarrow (iso\text{-}C_4H_9)_2NP(OC_6H_5)_2 + (iso\text{-}C_4H_9)_2NH\cdot HX \quad (13\text{-}28)$$

Similarly, compounds which can be classified as esters of phosphorodiamidites, $(R_2N)_2POR$, have been prepared.[70] The reaction in this case takes the following form

$$(R'O)PCl_2 + 4\ R_2NH \longrightarrow (R_2N)_2P(OR') + 2\ R_2NH\cdot HX \quad (13\text{-}29)$$

Orthophosphoromonamidates

The preparation of phosphoramidates first employed by Stokes[1] is probably the best method of making the pure inorganic derivatives. Phosphorus oxychloride is reacted with two moles of phenol to give a mixture of esters in which the monochlorophosphate, $(C_6H_5O)_2P(O)Cl$, predominates. This monochlorophosphate may first be separated from the other esters, or the entire mixture can be directly reacted with alcoholic ammonia according to the following equation.

$$(C_6H_5O)_2P(O)Cl + 2\ NH_3 \longrightarrow (C_6H_5O)_2P(O)NH_2 + NH_4Cl \quad (13\text{-}30)$$

The product from this reaction, diphenyl phosphoramidate, which is obtained in a yield of 35% based on the $POCl_3$ originally employed, can be saponified with a base to give the free phosphoramidate. When saponification is carried out with concentrated sodium hydroxide, the disodium salt, $Na_2O_3P(NH_2)$, is obtained, whereas saponification with ammonium hydroxide gives the ammonium salt of the monoester, $(NH_4)O_2P(NH_2)(OC_6H_5)$. The free acid is readily obtained in the form of microscopic crystals by precipitating the dibasic lead salt and treating it with hydrogen sulfide. It also can be made as a monohydrate by treating the monopotassium salt

[69] T. E. Thorpe and A. E. H. Tutton, *Trans. Chem. Soc.*, **59**, 1027 (1891).
[70] A. Michaelis, *Ann.*, **326**, 129 (1903).

with perchloric acid and precipitating with alcohol.[71] In addition, it has been prepared by use of an ion exchange resin.[71]

Phosphoramidic acid is very soluble in water but insoluble in alcohol. The aqueous solution has a sweetish taste and is hydrolyzed, after long standing at room temperature or rapidly in hot solution, into ammonium dihydrogen phosphate. Disodium phosphoramidate is also highly soluble in water and can be precipitated by alcohol from its aqueous solution as an oily liquid, which will crystallize if the container is scratched. The monosodium salt, $NaHO_3P(NH_2)$, can be obtained by the action of carbon dioxide on a solution of the disodium salt. It is sparingly soluble in cold water. On the other hand, the monoammonium and monopotassium salts are reasonably soluble in water.

Both the normal and the acid silver phosphoramidates are known in crystalline form. The normal salt, $Ag_2O_3P(NH_2)$, is obtained from an ammoniacal solution of silver nitrate; and the acid salt, $AgHO_3P(NH_2)$, from a silver nitrate solution acidified with nitric acid. Both silver salts are quite insoluble in water. Upon heating the various salts of phosphoramidic acid, ammonia and/or water are lost, and more condensed compounds are obtained. Details of this process will be discussed later.

The crystal structure of monosodium phosphoramidate, $NaHO_3P(NH_2)$, has been analyzed in detail by x-ray diffraction.[72] The structure shows that the phosphoramidate ion exists as a zwitter ion, $(NH_3{}^+PO_3{}^-)^-$, with the phosphorus atom being tetrahedrally surrounded by one nitrogen and three oxygen atoms. Each nitrogen is linked by three hydrogen bonds to the oxygen atoms in neighboring anions. The P-N distance is found to be 1.78 ± 0.03 A., and the P-O distance is found to equal 1.51 ± 0.02 A. The N—P—O angle equals 103°, and the O—P—O angle equals 115°. The measured P-O distance corresponds to about 0.6 π-bond per σ-bond, whereas the P-N distance is sufficiently large so that there appears to be no π-character in this bond as would be expected for an sp^3-hybrid of nitrogen.

The N-H-O distance is equal to 2.84 A., which can be compared with similar hydrogen-bond linkages in sulfamic acid, 2.82 A.; diketopiperazine, 2.85 A.; ammonium hypophosphite, 2.81 A.; and acetamide, 2.83 A. There are many similarities between the $(NH_3{}^+PO_3{}^-)^-$ ion and the zwitter ion, $NH_3{}^+SO_3{}^-$, present in crystals of sulfamic acid. It is interesting to note that the S-N distance in sulfamic acid also corresponds to a single

[71] R. Klement and K. H. Becht, *Z. anorg. Chem.*, **254**, 217 (1947); R. Klement, *ibid.*, **260**, 267 (1949); R. Klement, G. Biberacher, and V. Hille, *ibid.*, **289**, 80 (1957).

[72] E. Hobbs, D. E. C. Corbridge, and B. Raistrick, *Acta Cryst.*, **6**, 621 (1953).

bond, although the S-O distance is short as would be expected from a bond having considerable π-character.

Orthophosphorodiamidates

Phosphorodiamidates can be made from a phenyl chlorophosphate as are the phosphoromonamidates.[4] In this case, one mole of phenol is reacted with phosphorus oxychloride to give a product which is predominantly phenyl dichlorophosphate, $(C_6H_5O)P(O)Cl_2$. After purification by distillation, phenyl phosphorodiamidate is made from the dichlorophosphate by pouring the latter into an ice-cold solution of ammonia, containing about 25% NH_3. This reaction is accompanied by a crackling noise; and the yield of $(C_6H_5O)(O)P(NH_2)_2$, which is a white, granular solid, is 30–35%, based on the $POCl_3$ originally used. Saponification to the sodium salt is effected by mixing solid sodium hydroxide with the solid ester and adding water. The heat of solution of the sodium hydroxide starts the reaction from which $NaO_2P(NH_2)_2$ is obtained.

Sodium phosphorodiamidate is more readily prepared by heating phosphoryltriamide in 2 *N* sodium hydroxide on a water bath.[73] After about $^1/_2$ hr., the evolution of ammonia ceases, and the solution is filtered hot. Upon addition of acetone, the sodium phosphorodiamidate is precipitated as well-crystallized needles. Sometimes the precipitate comes out as an oil, but it can be crystallized by cooling to −30°C. and scratching the sides of the container. In this case, the tetrahydrate is obtained, $NaO_2P(NH_2)_2 \cdot 4\ H_2O$. Free phosphorodiamidic acid can be made by dissolving the sodium salt in an aqueous solution of acetic acid and then adding alcohol. The precipitate has the formula $HO_2P(NH_2)_2$.

The alkali metal salts of phosphorodiamidic acid are quite stable in water and are very soluble.[4] The barium and magnesium salts are quite soluble in water. Phosphorodiamidic acid is also moderately soluble in cold water. Unlike the phosphoromonamidic acid, which has a sweetish taste, phosphorodiamidic acid has a decidedly sour flavor. Presumably, it is only partially present in aqueous solution as a zwitter ion, $(NH_3^+)(NH_2)$-PO_2^-. Phosphorodiamidates can be distinguished from phosphoromonamidates by boiling with an excess of barium hydroxide. The phosphoromonamidate ion undergoes nearly instantaneous decomposition to the simple orthophosphate in this case, whereas the phosphorodiamidate ion is only slowly decomposed (about 5% per hr.).

Stokes[4] has shown that evaporation of solutions of the alkali metal or al-

[73] R. Klement and O. Koch, *Chem. Ber.*, **87**, 333 (1954).

kaline earth metal salts of phosphorodiamidic acid results in the formation of vitreous masses which are presumably noncrystalline. This is true whether there are one or more equivalents of cation per phosphorodiamidate ion. An interesting behavior is observed with the silver derivatives.[4] The normal salt, $AgO_2P(NH_2)_2$, is a white, stable substance which can be prepared as relatively large, well-formed, prismatic crystals by dissolving in ammonia and slowly evaporating the ammonia from the solution. In addition, it is possible to make silver precipitates in which the Ag/P mole ratio is greater than unity, going as high as 5 These compounds exhibiting high Ag/P ratios are obtained from alkaline solutions. For an Ag/P mole ratio of 2, the precipitate appears to be in the form of white curds. For Ag/P = 3, the precipitate is yellow-colored in most cases but can exhibit deep red color, depending on preparative details.[4] For Ag/P = 4, the precipitate has a reddish brown coloration; and, for Ag/P = 5, the precipitate is a dark brown amorphous substance, which readily detonates from mechanical action when dry. Klement *et al.*[73] concluded in 1957, on the basis of its reaction with no more than four moles of methyl iodide per mole of contained phosphorus and the subsequent isolation of $(CH_3)_2N$— groups, that the precipitate for which Ag/P = 5 has the formula $AgO_2P(NAg_2)_2$.

If a 30% solution of potassium hydroxide is poured on the crystalline silver salt, $AgO_2P(NH_2)_2$, a white, pasty mass results, which swells up to a transparent gel upon being mixed with water If allowed to stand, this gel begins to grow turbid and after several hours deposits a voluminous snow-white mass in which the Ag/P mole ratio is equal to about 2. If the gel is greatly diluted in water, the solution first takes on a yellowish tint and finally exhibits a deep wine-red color. This transparent wine-red solution corresponds to a very small concentration of the silver phophoramidate, *e.g.*, 1 g./l. The chemistry of the action of alkalies on phosphorodiamidates should be reinvestigated with modern techniques and in the light of present-day theory. Particularly, the constitution of the silver derivatives is worth additional study

Organic Derivatives of Phosphoramidates

Primary and secondary organic amines, RNH_2 and R_2NH react with phosphoryl halides, substituted phosphoryl halides, organic halophosphates, and halophosphoramidates to form the corresponding amides. The reactions are carried out in inert solvents, such as ether or ligroin, at low or moderate temperatures, and the products are isolated after removal of the amine salt by filtration Typical reactions[34] are as follows:

$$POCl_3 + 2\,RNH_2 \longrightarrow (RNH)P(O)Cl_2 + RNH_2 \cdot HCl$$
$$POCl_3 + 4\,RNH_2 \longrightarrow (RNH)_2P(O)Cl + 2\,RNH_2 \cdot HCl \qquad (13\text{-}31)$$
$$(R'O)P(O)Cl_2 + 4\,RNH_2 \longrightarrow (R'O)P(O)(NHR)_2 + 2\,RNH_2 \cdot HCl$$

Usually a mixture of products is obtained, but the degree of substitution can be approximately controlled by using the proper proportion of reagents. The use of phosphoryl dichlorofluoride, $OPFCl_2$, gives replacement of the chlorine by the amido groups with essentially no action on the fluorine atom.[74] Free acids are made from the chloro derivatives by hydrolysis of the chlorine atom. Thus, the two chlorophosphoramidates shown as products in equations 13-31 hydrolyze to $H_2O_3P(HNR)$ and $HO_2P(HNR)_2$, respectively.

Instead of employing the free organic amine, it is also possible to use an amine hydrogen chloride in reactions with $POCl_3$. This procedure is most commonly applied to the preparation of dichlorophosphoramidates from primary amines or occasionally to the preparation of chlorophosphorodiamidates. When the amine hydrogen chloride is used, the reactions are carried out by refluxing until the suspended amine salt disappears to give a clear solution. At that time, the heating must be stopped, since additional heating leads to imido derivatives. As would be expected, thio compounds can be made by substituting thiophosphoryl halides or their derivatives for the phosphoryl halides in the reactions shown in 13-31. Thio derivatives can also be made[70] by the following reaction and its variations.

$$(R_2N)_2POR' + S \longrightarrow (R_2N)_2P(S)OR' \qquad (13\text{-}32)$$

Another interesting reaction[70] in which sulfur dioxide reacts with organic polyhalides is the following.

$$R_2NPCl_4 + SO_2 \longrightarrow R_2NP(O)Cl_2 + SOCl_2 \qquad (13\text{-}33)$$

A number of other reactions for the preparation of organic derivatives of the phosphoramidates are given by Kosolapoff.[34]

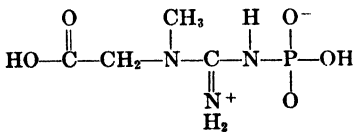
The properties of typical organic derivatives of the phosphoramidates are given in Table 13-6. A much larger listing is presented by Kosolapoff.[34] Several organic phosphoramidates play a role in biology. The most important of these are creatine phosphate and arginine phosphate. These two substances, which are also known as phosphocreatine and phosphagine, serve as energy-storage compounds for the muscles, with creatine phosphate being found in vertebrates and arginine phosphate in invertebrates. By

[74] R. Heap and B. C. Saunders, *J. Chem. Soc.*, **1948**, 1313; H. McCombie and B. C Saunders, Nature, **157**, 776 (1946).

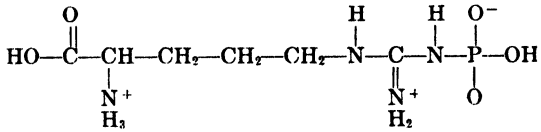
TABLE 13-6
Some Organic Derivatives of Phosphorus-Based Acids Having N—P Bonds

Compound	Properties
$[(C_2H_5)_2N]_2P(OC_2H_5)$	b.p.$_{23\ mm.}$ = 105–108°C.
$(C_6H_5O)P(NH_2)O_2H$	m.p. of cinchonine salt = 194°C.
$(C_6H_5O)P(NH_2)_2OH$	Isolated as salts
$(C_6H_5O)_2P(NH_2)(O)$	m.p. = 147°C.
$(C_6H_5O)_2P(NH_2)(S)$	m.p. = 113°C.
$(C_6H_5O)_2P(NHC_6H_5)(O)$	m.p. = 129°C.
$(C_6H_5O)_2P(NHC_6H_5)(S)$	m.p = 92°C.
$(C_6H_5O)_2P[N(C_6H_5)_2](O)$	m.p. = 180°C.
$(C_6H_5NH)P(NH_2)O_2H$	m.p. = 158°C.
$(C_6H_5O)P(NH_2)_2(O)$	m.p. = 184°C.
$(C_6H_5O)P(NH_2)_2(S)$	m.p. = 119°C.
$[(CH_3)_2N]_2PO(OC_6H_5)$	b.p.$_{0.5\ mm}$ = 160°C.
$(C_6H_5NHNH)_2POH$	Solid, decomp. at 80°C.
$(C_6H_5O)P(NHNH_2)O_2H$	
$(C_6H_5O)_2P—N—N—P(OC_6H_5)_2$ (H H)	Crystalline

means of an enzymatic reaction, these compounds act to phosphorylate adenosine diphosphate to adenosine triphosphate so that the latter can contribute immediate energy to the muscle.[75] The formulas of these two compounds are given below in the zwitter-ion form in which they exist in acidic solution.

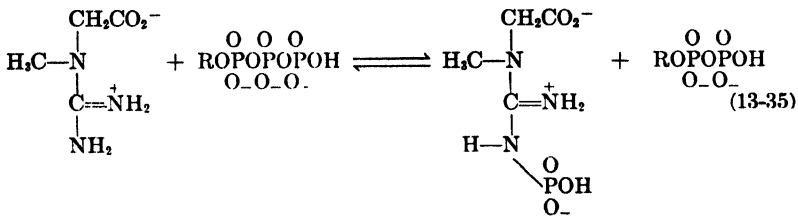


creatine phosphoric acid



arginine phosphoric acid (13-34)

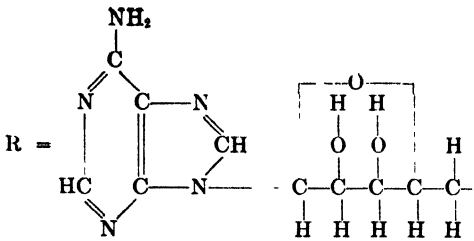
The reversible equation[76] for the phosphorylation of creatine by adenosine triphosphate is shown below:



(13-35)

[75] A. G. Szent-Györgyi, *Advances in Enzymol.*, **16**, 346 (1955).

where



There is believed to be a particular transphosphorylating enzyme, called creatine kinase,[76] which catalyzes the reaction shown in equation 13-35. The equilibrium is shifted to the left at pH values more acid than pH 8.55, at which value the equilibrium constant for equation 13-35 equals 0.04. Generally speaking, a number of phosphoamidases catalyze the transfer of the phosphoryl moiety from creatine phosphate to various acceptors. Thus, an enzyme from intestinal mucosa catalyzes the phosphorylation of glucose, glycerol, or fructose by phosphocreatinine.[77] Phosphoamidases from other sources, such as the prostate, also catalyze these reactions. Separation of a phosphoamidase from a phosphomonoesterase having a similar pH optimum has been effected by selective sorption of the latter on kaolin.[78] At present, two phosphoamidases have been quite well characterized.[79] One has a pH optimum for catalytic activity at pH 9, the other at pH 5.2. There may be a third phosphoamidase[79] with a pH optimum near pH 3.0.

Cyclic Metaphosphimates

When the phosphonitrilic chlorides described in Chapter 6 are hydrolyzed, a series of cyclic imidoacids are obtained.[5,80] The most recent names given to these acids are the metaphosphimic acids, with the number of phosphorus atoms in the ring being denoted by the prefixes: tri, tetra,

[76] L. Lorand, *Nature*, **172**, 1181 (1953); I. Banga, *Studies Inst. Med. Chem. Univ. Szeged*, **3**, 59 (1943); J. K. Parnas, C. Lutwak-Mann, and T. Mann, *Biochem. Z.*, **281**, 168 (1935); H. Lehmann, *ibid.*, **286**, 336 (1936).

[77] O. Meyerhof and H. Green, *J. Biol. Chem.*, **183**, 377 (1950); *ibid.*, **197**, 347 (1952); R. K. Morton, *Nature*, **172**, 65 (1953).

[78] M Ichihara, *J. Biochem. (Japan)*, **18**, 87 (1933).

[79] E. Waldschmidt-Leitz and F. Köhler, *Biochem. Z.*, **258**, 360 (1933); J. Roche and J. Baudoin, *Compt. rend. soc. biol.*, **137**, 245 (1943); H. Bredereck and E. Geyer, *Z. physiol. Chem.*, **254**, 223 (1938).

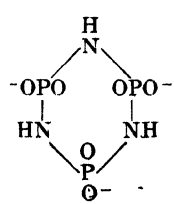
[80] A. Laymann, "Die Metaphosphimsaüren und ihre Salze," Ph.D. Thesis, Munich, Germany, 1931; A. M. de Ficquelmont, *Compt. rend.*, **202**, 423 (1936); *Ann. chim.*, **12**, 169 (1939).

etc.—as in trimetaphosphimic acid. These acids are also called phosphonitrilic acids or imidometaphosphoric acids.

Sodium trimetaphosphimate is readily prepared[5] by saponification of an ether solution of the trimer of phosphonitrilic chloride, $(PNCl_2)_3$, through contact with an aqueous sodium acetate solution. In detail, this preparation is carried out by dissolving 30 g. of $(PNCl_2)_3$ in 150 ml. of alcohol-free ethyl ether. This solution is then contacted with an aqueous solution prepared by adding 110 g. of sodium acetate to 200 ml. of water The two immiscible solutions are agitated together for 85–100 hr. by sealing them into a bottle clamped on a rotating framework. During this period, the salt $Na_3(PNO_2H)_3 \cdot 4\ H_2O$ crystallizes out of the aqueous phase.

Tetrameric phosphonitrilic chloride hydrolyzes more readily than does the trimeric variety, so that water or ammonium hydroxide can be used in place of the sodium acetate solution employed in hydrolyzing the trimer Thus, when $(PNCl_2)_4$ in 15 volumes of ether is shaken with 5 volumes of water, needles of the dihydrate of tetrametaphosphimic acid, $(PNO_2H_2)_4 \cdot 2\ H_2O$, begin to form in $^1/_2$ hr., and after 20 hr. the aqueous phases consist of a pasty mass of these crystals suspended in a solution of hydrochloric acid. The higher homologs in the series of cyclic metaphosphimates can be prepared in the same manner as is used in making the trimetaphosphimates.

Preliminary x-ray structural data on tetrametaphosphimic acid and some of its salts indicate that the anion consists of a puckered, eight-membered ring of alternate phosphorus and nitrogen atoms similar to that found in the parent phosphonitrilic chloride.[81] Stokes[5] and later workers found that one hydrogen per phosphorus atom in the cyclic metaphosphimic acids could be substituted by a metal so as to form a salt. Moreover, when less than one hydrogen per phosphorus was substituted by a metal ion, the resulting salt exhibited acidic properties. This led Stokes to the conclusion that of the two hydrogens in $PN(OH)_2$ polymers, one was directly attached onto the nitrogen atom, as shown below for the cyclic trimer



(13-36)

This structure is quite reasonable, in that there are two oxygen atoms to bear the single negative charge, so that the detailed electronic structure of

[81] D. E. C. Corbridge, *Acta Cryst.*, 6, 104 (1953).

the phosphorus atom and the bonds to its tetrahedron of neighboring atoms is probably quite similar to that existing in the hypophosphite ion, $(H_2PO_2)^-$, or a phosphate middle group, $-OP(O_2^-)O-$. Stokes' findings as to salt formation are borne out by the titration curve of tetrametaphosphimic acid, shown in Figure 13-9. Although only the first three hydrogen atoms in trimetaphosphimic acid are strongly acidic and readily substituted by a metal ion through reaction with a base, Stokes did prepare a rather "unstable" tetrasodium derivative, $Na_4H_2(PNO_2)_3(?)$, which he crystallized from a strong solution of sodium hydroxide. Stokes also made a

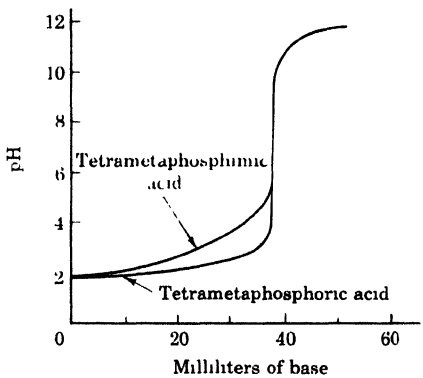


Fig. 13-9 Titration curve of tetrametaphosphimic acid compared to that of tetrametaphosphoric acid. The end point at pH equal to about 7 corresponds to one equivalent of base per atomic weight of phosphorus

number of silver derivatives in which the Ag/P mole ratio was greater than unity. However, the monosilver salt, $Ag_3H_3(PNO_2)_2$, was crystalline, whereas the trimetaphosphimates in which the Ag/P mole ratio was greater than unity were described as amorphous. A silver derivative in which Ag/P = 2 was also reported for the tetrametaphosphimic acid.[5] Study of esterification of the silver derivatives with ethyl iodide indicate that the ethoxy groups can be attached both to the nitrogen and to the oxygen atoms in the cyclic structures.[82]

The hydrolysis of the trimetaphosphimate ion in neutral solution is a rather complex process,[83] as indicated in Figure 13-10. The most interesting part of this process is the stepwise substitution of oxygen atoms for the

[82] R. Ratz and M. Hess, *Ber.*, **84**, 889 (1951).

[83] A. Narath, F. H. Lohman, and O. T. Quimby, *J. Am. Chem. Soc.*, **78**, 4493 (1956); E. Thilo and R. Rätz, *Z. anorg. Chem.*, **258**, 33 (1949).

ring nitrogens without splitting the ring! Apparently the structure of the activated complex is such that an oxygen bridge forms between a pair of phosphorus atoms before there is rupture of the nitrogen bridge based on the imido group.

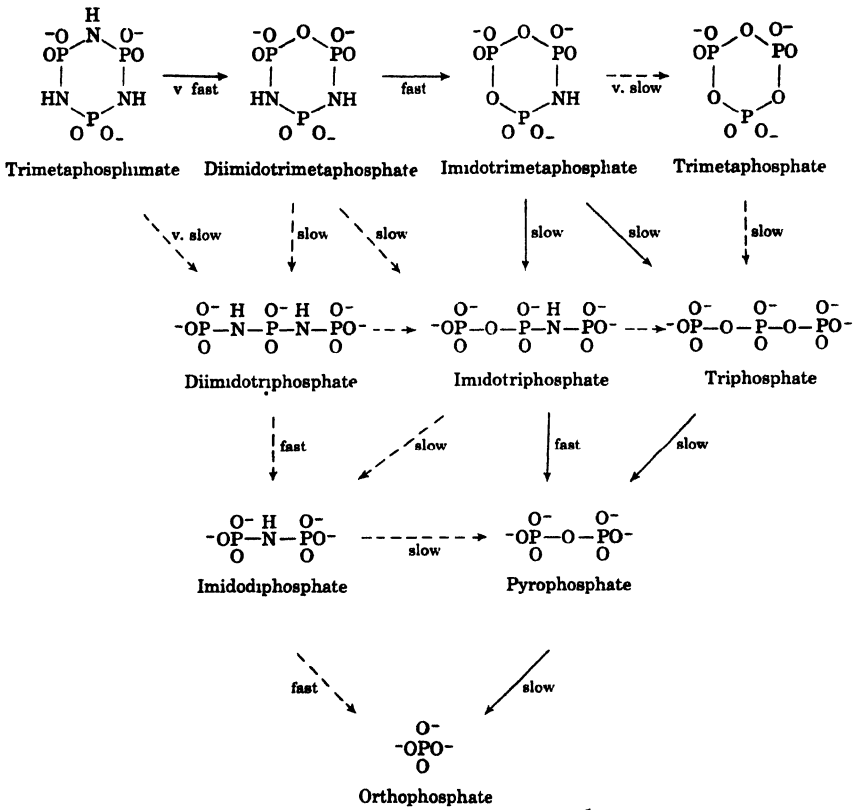


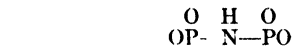
Fig. 13-10. Scheme of hydrolysis of the trimetaphosphimate anion.

Chain Amido- and Imidophosphates

Although the early literature describes a number of phosphates that are presumably chains in which various oxygen atoms have been substituted by nitrogen-based groups,[84] it is very difficult to determine whether or

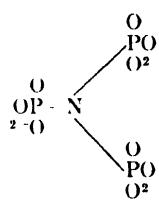
[84] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1940, Vol. VIII; R. Dubrisay, *Traité de Chimie Minérale*, ed. Paul Pascal, Masson, Paris, 1932, Vol. III, pp. 346–528.

not pure compounds are involved and whether the compounds, if pure, really exhibit the structure ascribed to them. In a recent series of papers by Klement and Biberacher,[85] several amido and imido chain phosphates have been reasonably well characterized by modern methods, including paper chromatography. One of the salts which has been quite well established is sodium pyrophosphorimidate, which can also be called sodium imidodiphosphate. This was prepared by heating anhydrous sodium acid phosphoramidate in a vacuum at 80°C. for 6 hr. The impure product thus obtained was purified by fractional crystallization to give the tetrasodium salt of the following anion.



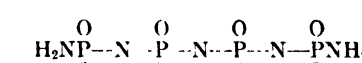
(13-37)

By heating anhydrous sodium acid phophoramidate to 80°C. in a vacuum in order to make the crude tetrasodium pyrophosphorimidate, and then further heating this for several days at 450°C., also under vacuum, a compound having the formula $Na_6P_3O_9N$ was obtained. The anion corresponding to this salt is postulated to have the following form.



(13-38)

By heating sodium phosphorodiamidate at 160°C. under vacuum, a mixture of condensed amido-imidophosphates is formed. By heating at higher temperatures, a mixture of even more condensed structures is formed. A study based on paper chromatography indicates that there are a number of separable amido-imidophosphates. One such compound is shown below.



(13-39)

It appears from the chromatographic data that homologs ranging from the monomer to the hexamer have been separated in trace amounts.

A range of products resulting from the reaction of ammonia, water, and phosphorus pentoxide can be classed as chain phosphates having some

[85] R. Klement and G. Biberacher, *Z. anorg. u. allgem. Chem.*, **283**, 246 (1956); *ibid.*, **285**, 74 (1956); G. Biberacher, *ibid.*, **285**, 86 (1956).

amido and imido groups.[86,87] These materials can be prepared in a number of ways. The most versatile is to react a controlled mixture of ammonia and water vapors with a hot stream of P_4O_{10} vapor in dry air, with the P_4O_{10} having been made from the burning of phosphorus in the same apparatus. Nearly immediately after mixing the ammonia and water with the phosphorus pentoxide vapor, the gas stream is quenched.[86] Product characteristics and composition are controlled by adjusting (1) the $NH_3/H_2O/P_2O_5$ ratio, (2) the temperature of the P_4O_{10} vapor, and (3) the time interval between mixing the NH_3 and H_2O with the P_4O_{10} and quenching the product. Other preparations consist of adding phosphorus pentoxide to liquid ammonia or passing ammonia plus perhaps *some* water vapor over solid phosphorus pentoxide. Unless the $NH_3/H_2O/P_2O_5$ ratio corresponds quite closely to that of the ammonium orthophosphates, the products are usually amorphous or show only a few x-ray diffraction lines belonging to the ammonium orthophosphates. Throughout most of the region of composition corresponding to an NH_3/P_2O_5 mole ratio between 0.8 and about 3 and an H_2O/NH_3 mole ratio between 0 and about 2, the product is an amorphous white material—a significant fraction of which may be insoluble or slowly soluble in water. Study of these products shows that they are rather complicated mixtures of a number of different molecule-ions. The products obtained from quenching the vapors are often acidic in aqueous solution However, by a subsequent calcination in ammonia vapor, the acid functions can be neutralized

If we assume no rings are produced and that there are no P—P bonds and all of the phosphorus is quadruply connected, the compounds formed by reaction of phosphorus pentoxide with ammonia plus more or less water exhibit the general formula: $(N_w'H_x)P_nO_yN_z$, in which N′ is the ammonium nitrogen (not directly bonded to the phosphorus) and N is the nitrogen (H_2N—, —NH—, and —N<) attached to the phosphorus. The number-average number of phosphorus atoms per molecule-ion will then be

$$\bar{n} = \frac{1}{(y + z)/(n) + 3} \qquad (13\text{-}40)$$

[86] P. G. Arvan, J. H. Payne, G. Muchow *et al.*, private communications from the Monsanto Chemical Co.; also O. C. Jones and P. G. Arvan, U. S. Pat. 2,717,198 (1955, assigned to Monsanto Chemical Co.).

[87] H. Fisher, *Über Reaktionsprodukte aus Phosphorpentoxyd und Ammoniak und deren Eignung zur Wasserenthartnung*, M. Dittert, Dresden, 1941; A. Sanfourche, A. Hernette, and M. Fau, *Bull. soc. chim.*, **47**, 273 (1930); L. Harris and C. B. Wooster, *J. Am. Chem Soc.*, **51**, 2121 (1929); J. Sancho and E. Moles, *Annales soc. españ. fis. y quím.*, **30**, 701 (1932); W. H. Woodstock, U. S. Pat. 2,122,122 (1938, assigned to Victor Chem. Works), Ger. Pat. 735,162 (1943); and others.

in which, from the material balance, we see that $NH_3 = w + z$, $x = 3NH_3 + 2H_2O$, $n = 2P_2O_5$, and $y = H_2O + 5P_2O_5$.

By substituting the values for n, y, and z into equation 13-40, we obtain the following equation in which the average number of phosphorus atoms per molecule-ion is related to the over-all composition

$$\bar{n} = \frac{2}{(H_2O + \text{nonammonium-N})/(P_2O_5) - 1} \qquad (13\text{-}41)$$

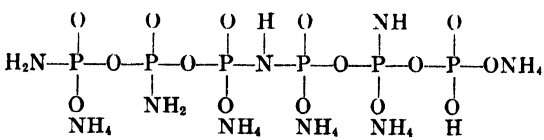
This equation is found to agree with average molecular weights determined from the nuclear magnetic resonance spectra, in which ortho(phosphates or amidates), end groups, middle groups, and branching points exhibit separate resonance peaks.

From equation 13-41, it is obvious that only nitrogen directly bonded to the phosphorus influences the molecular size, so that neutralization of an acid group with ammonia to form an ammonium salt has no effect. The over-all equation for the reaction is seen to be

$$(w + z)NH_3 + (n/2)P_2O_5 + (y - 5n/2)H_2O \longrightarrow (N_w{}'H_{3w+3z+2y-5n})P_nO_yN_z \qquad (13\text{-}42)$$

where $y \geqslant 5n/2$, and $(y + z)/n \geqslant 4$.

In a typical reaction product, an individual molecular species corresponding to the empirical composition, $9NH_3 \cdot 3P_2O_5$, might exhibit the following structure:



(13-43)

TIN AND ARSENIC ANALOGS OF PHOSPHONIC ACIDS

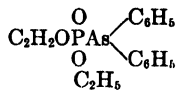
About a dozen compounds in which there is believed to be an Sn—P bond have been made by reacting tertiary esters of phosphorous acid with alkyl tin halides.[88] Typical examples of these compounds are shown below.

(13-44)

Similarly, arsenic derivatives have been prepared in which there is an

[88] B. A. Arbusov and N. P. Grechnik, *Zhur. obshchet Khim.*, **17**, 2166 (1947); B. A. Arbusov and A. N. Pudovik, *ibid.*, **17**, 2158 (1947).

As—P bond.[89] In all of the seven known compounds in this class, there is only one phosphorus and one arsenic atom per molecule. An example is given below.



(13-45)

[89] G. X. Kamai and O. N. Belorossova, *Izvest. Akad. Nauk S.S.S R., Otdel. Khim. Nauk*, **1947**, 191.

APPENDIX A

Phosphate Minerals

In the following table are listed the 187 accepted mineral names which are given for phosphates in Volume II of *Dana's System of Mineralogy*, 7th ed. (edited by E. Palache, H. Berman, and C. Frondel), John Wiley & Sons, N. Y., 1951. In addition to the name, the chemical formula, some crystallographic data, and the associated minerals are listed. When the mineral has been synthesized in the laboratory, a brief description of the synthesis is presented. Additional information on all of the factors listed, as well as on other items, can be obtained by referring to the proper page of Dana, Vol. II, as given in this table.

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana Vol. II
Monetite	$[CaH(PO_4)]_4$	Triclinic, pinacoidal-1.	Analyses of pure natural material are lacking Soluble in acids.	Obtained in crystals by heating precipitated $CaHSO_4 \cdot 2\,H_2O$ with water in a closed tube at 150°, by slow interdiffusion of Na_2HPO_4 and $CaCl_2$ solutions, and in numerous other ways.	Occurs with gypsum and whitlockite; also with apatite and newberyite	pp. 660–61
Triphylite Lithiophilite	$[Li(Fe'', Mn'')PO_4]_4$	Orthorhombic, dipyramidal. Space group *Pmna* if holohedral	A phosphate of lithium and divalent Fe and Mn; Fe'' and Mn'' substitute mutually, and a complete series extends between triphylite and lithiophilite. Soluble in acids	Crystals of $LiMn''PO_4$ have been obtained by heating LiCl and $MnCl_2$ in a stream of $POCl_3$ and water vapor at 850°, and also by melting together LiCl, $Li_3(PO_4)$ and $Mn_3(PO_4)_2$. See Zambonini and Malossi, *Z. Krist.* **80**, 442 (1931).	These two are common minerals and occur as primary minerals in granite pegmatites. Commonly associated species include triploidite-wolfeite, eosphorite, spodumene, albite, beryl, amblygonite, and graftonite	pp. 664–69
Hühnerkobelite Varulite	$(Na, Ca)(Fe'', Mn'')_2(PO_4)_2$	Probably orthorhombic.	A complete series probably exists between hühnerkobelite and varulite		A primary mineral found in granite pegmatites; also as a hydrothermal alteration product of triphylite Uncommon.	pp. 669–70
Natrophilite	$[Na\ MnPO_4]_4$	Crystal structure related to but not identical with that of triphylite-lithiophilite. Space group *P mna* if holohedral	A phosphate of Na and Mn. Fe ''substitutes for Mn'', with Fe: Mn $\approx$1:13 in the only reported analysis. Soluble in acids.		Known only from a single occurrence. Found sparingly with lithiophilite, triploidite, esophorite, in granite pegmatites	pp 670–71

Ferri-Sicklerite **Sicklerite**	$[(Li, Mn'' Fe''')PO_4]_4$	Orthorhombic	Formed as alteration products of triphylite lithiophilite Easily fusible Soluble in acids		See triphylite and lithiophilite above	pp. 672–73
Alluaudite	$(Na, Fe''', Mn'')(PO_4)$		Parent varulite-huhnerkobelite and these minerals are derived by oxidation of the Fe'' (see sicklerite). Soluble in acids		Secondary minerals In pegmatites	pp. 674–75
Mangan-Alluaudite	$(Na\ Mn'', Fe''')(PO_4)$					
Heterosite **Purpurite**	$[(Fe''', Mn''')PO_4]_4$	Orthorhombic	Secondary minerals formed by oxidation of triphylite and lithiophilite through the intermediate stage of ferrisicklerite and sicklerite Easily soluble in HCl.			pp. 675–77
Beryllonite	$[Na\ Be\ PO_4]_{12}$	Monoclinic prismatic with marked orthorhombic pseudosymmetry. Space group $P\ 2_1/c$	Slowly soluble in acids	Obtained in hexagonal tablets or prisms by slow cooling of a fusion of BeO and NaCl in sodium pyrophosphate or of BeO in sodium metaphosphate. See Ouvrard, *Compt rend* **110, 1334 (1890).**	In pegmatites	pp. 677–79
Arrojadite	$[Na_2(Fe'',Mn'')_6(PO_4)_4]_{12}$	Monoclinic; prismatic Space group $C2/m$ if holohedral	**Significant amounts of K and Ca substitute for Na; Mg, Al are present in substitution for (Fe'', Mn''). Soluble in dilute acids.**		Found in pegmatite See triphylite & lithiophilite.	pp. 679–81

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol II
Whitlockite	$[Ca_3(PO_4)_2]_7$ in the rhombohedral unit	Hexagonal-R; scalenohedral. Space group probably $R\bar{3}c$.	Analogous to carbonate-apatite. Whitlockite is dimorphous but the alpha polymorph is not known to occur in nature. Easily soluble in dilute acids	Observed in certain slags	Associated with siderite, quartz, apatite, etc., as hydrothermal mineral. Some in Curaçao phosphate rock.	pp. 684–86
Graftonite	$[(Fe'', Mn'', Ca)_3(PO_4)_2]_4$	Monoclinic; prismatic Space group $P2_1/c$.	A limited isomorphous series extends between Fe, Mn, and Ca Graftonite is not isostructural with whitlockite, caryinite, or fillowite.		Found as a primary mineral in complex granite pegmatites	pp. 686–87
Xenotime	$[Y\,PO_4]_4$	Tetragonal; ditetragonal-dipyramidal Space group $I4/amd$.	Yttrium is sometimes substituted in considerable part by Er and, in lesser amount, by other rare earths such as Ce, La, Sc Hardly attacked by hot acids	In crystals by fusion of precipitated yttrium phosphate in potassium sulfate, borax, or salts of phosphorus; also by fusion of yttrium oxide with potassium pyrophosphate See Radominski, *Compt. rend*, **80**, 304 (1875); Duboin, *ibid.* **107**, 622 (1888); and Florence, *Jb. Mineral* **2**, 139 (1908)	Commonly associated minerals include monazite, zircon, rutile, anatase, magnetite, ilmenite, hematite, sillimanite, alkalic feldspars, and less commonly, fergusonite and other columbate-tantalates.	pp. 688–91

Monazite	$[(Ce, La, Y, Th)PO_4]_4$	Monoclinic; prismatic. Space group $P\ 2_1/n$	A phosphate essentially of the Ce metals. Th is usually present in substitution for (Ce, La) The amount of Th present ranges from a few weight per cent of ThO_2 to 10 or 12% but a series probably extends up to at least 30%; —Th free material is rare. U has been reported in amounts up to 1 wt -% U_3O_8	In crystals by fusion of admixed phosphate and chloride of cerium See Radominski, *Compt. rend.*, **80**, 304 (1875)	Associated minerals include zircon, xenotime, gadolinite, samarskite, fergusonite, magnetite, apatite, columbite, ilmenite	pp. 691–96
Berlinite	$[Al\ PO_4]_3$	Hexagonal-R trigonal-trapezohedral Space group $C3_12$ = $C3_22$. Isostructural with $Al(AsO_4)$. Isotypic with α-SiO_2, quartz	The only reported analysis on natural material apparently was made on a sample containing adsorbed, nonessential water or an admixed hydrated aluminum phosphate Easily soluble in alkalies but not in acids	Obtained as crystals from solution in phosphoric acid. Berlinite or the tridymite-like or cristobalite-like polymorphs thereof are obtained by heating hydrated aluminum phosphates. See Manley, *Am Mineralogist*, **35**, 108 (1950)	Found with augelite, attacolite, and other phosphates in Sweden	pp. 696–97
Stercorite	$Na(NH_4)HPO_4 \cdot 4H_2O$	Triclinic; pseudomonoclinic.	The reported analyses of natural material do not conform closely to the cited formula (microcosmic salt). Soluble in water. On heating, NH_3 is lost at about 200°C.	Obtained as crystals by evaporation of a water solution of the salt, preferably in the range from +10° to −6°C. (below which point another phase appears).	Found in guano on islands off Peru and West Africa.	pp. 698–99
Hannayite	$Mg_3(NH_4)_2H_4(PO_4)_4 \cdot 8H_2O$	Triclinic; pinacoidal-$\bar{1}$ (?).	Loses 21% H_2O between 100° and 115° and the remainder at a high heat Easily soluble in acids before fusion.		Found with struvite, brushite, newberyite, dittmarite, bobierrite (?) and schertelite in bat guano in Australia.	pp. 699–700

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Hureaulite	$[Mn_5H_2(PO_4)_4 4H_2O]_4$	Monoclinic; prismatic-2/*m*. Space group $P2'/c$.	Fe'' substitutes for Mn'', and a series extends from at least Fe:Mn = 1·3.0 down to Fe Mn = 1.9.4 and probably to the pure Mn compound. Easily soluble in acids	Obtained as crystals by neutralization with ammonia of a solution of manganese phosphate The Cd analog has also been prepared. See de Schulten, *Bull soc ind minérale St. Etienne*. **27**, 123 (1904)	Found with vivianite and rockbridgeite and other associated minerals formed by the alteration of triphylite and lithiophilite	pp 700–02
Wenselite		Monoclinic; prismatic-2/*m*.	A hydrated acid phosphate of Mn, Mg, and Fe of uncertain formula, approximately as follows· (Mn, Mg, Fe) $H(PO_4)$ $2H_2O$.		Probably identical with hureaulite	pp 702–03
Baldaufite		Monoclinic.	Closely resembles wenselite. Possible composition is $H_2(Fe, Mn, Ca, Mg)_5(PO_4)_4$ $5H_2O$		Found with dufrenite in a phosphate-bearing pegmatite	pp 703
Brushite	$[CaHPO_4 2H_2O]_4$	Monoclinic, sphenoidal-2. Space group probably *A*2.	Some analyses show variations in water content Loses water readily even at ordinary temperature, eventually turning to $CaHPO_4$, monetite Readily soluble in HCl Some habits resemble gypsum	Formed by precipitation from a calcium chloride solution by sodium acid phosphate May be grown in crystals by slow evaporation of an acetic acid solution of calcium phosphate. Data on the system $CaO–H_2O–P_2O_5$ are given in Ch 9	Widespread in phosphate deposits. Often formed on old bones	pp 704–06

Newberyite	$MgH(PO_4)\ 3\ H_2O$	Orthorhombic, dipyramidal.	Barely soluble in cold water, dissolves in acids	May be formed by dehydration of $MgHPO_4\ 7\ H_2O$ at ordinary temperatures. Crystallized from a solution of $MgHPO_4\ 7\ H_2O$ in 25% acetic acid evaporated on a steam bath and in a variety of other ways between room temperature and 150°C. Can be crystallized together with struvite at ordinary temperature. In the system $MgO–P_2O_5–H_2O$ at 25°C., the trihydrate is the only stable hydrate of $MgHPO_4$. See Hägele and Machatschki, *Centr. Mineral. Geol.*, **1939A** 297 (1939); de Schulten, *Bull soc. ind. minérale St Étienne*, **26**, 24 and 95 (1903); and Cameron and Bell, *J. Phys Chem.*, **11**, 317 (1907).	In several caverns	pp. 709–10
Phosphorroesslerite	$[MgHPO_4 \cdot 7\ H_2O]_2$	Monoclinic; prismatic Space group $A2/a$	Isostructural and probably isomorphous with roesslerite. Slightly soluble in water, soluble in acids.	Crystallizes in needles [010] with the forms {010} {120}, {140}, and {$\bar{1}$11} when a magnesium sulfate solution is precipitated by phosphate ions at room temperature. In the system $MgO–P_2O_5–H_2O$, $MgHPO_4 \cdot 7\ H_2O$ does not appear at 25°C. See Cameron and Bell, *J. Phys. Chem.*, **11**, 363 (1907)	Related mineral roesslerite, of which it is the phosphate analog.	pp. 713–14

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Struvite	$[Mg(NH_4)PO_4 6H_2O]_2$	Orthorhombic; pyramidal. Space group $Pmc2$.	Small amounts of Mn'' and Fe'' substitute for Mg. Very slightly soluble in water (0.05 g. in 100 ml. H_2O at 20° C.) and dissolves in acids.	Formed as a precipitate in the analytical determination of magnesium or phosphorus. Obtained in large crystals by slow reaction of magnesium sulfate solution with an acid solution of ammonium phosphate.	Found with newberyite in the Yukon and with brushite in caves on the Island of Reunion. Large crystals sometimes form in canned fish.	pp. 715–17
Dickinsonite	$[H_2Na_6(Mn, Fe)_{14}(PO_4)_{12} H_2O]_4$	Monoclinic; prismatic Space group $C2/c$	Divalent Fe, Ca, and Mg substitute for Mn Soluble in acids.		In pegmatites associated with eosphorite, triploidite, lithiophilite, rhodochrosite, reddingite, fairfieldite.	pp. 717–719
Fillowite		Monoclinic	The exact formula is uncertain and, as given differs from that of dicksonite only in the ratio of the divalent cations. Possible formula is $H_2Na_6(Mn, Fe, Ca)_{14}(PO_4)_{12} H_2O$.		In pegmatites associated with triploidite, fairfieldite, and reddingite	pp. 719–20
Fairfieldite	$[Ca(Mn, Fe)PO_4 H_2O]_2$	Triclinic, pinacoidal-$\bar{1}$ Space group $P\bar{1}$	Fe'' substitutes for Mn'' Soluble in acids		In pegmatites associated with eosphorite, triploidite, dickinsonite, reddingite, fillowite, and lithiophilite.	pp. 720–22
Collinsite	$[Ca(Mg, Fe)(PO_4) H_2O]_2$	Triclinic, pinacoidal-$\bar{1}$ (?). Space group $P\bar{1}$	Fe'' substitutes for Mg Easily dissolved in acids		Asphaltum	pp. 722–23

Reddingite **Phosphoferrite**	$[(Mn, Fe)_3(PO_4)_2 \cdot 3\,H_2O]_4$	Orthorhombic; dipyramidal. Space group *Pmna*.	Mn'' and Fe'' substitute mutually, and a series extends from at least Fe·Mn = 1·22 to at least Fe Mn = 2.7.1. Soluble in acids.	A hydrated manganese phosphate perhaps identical with reddingite. Has been obtained by reaction of manganous carbonate with excess phosphoric acid. See Debray, *Ann. chim. et phys*, **61**, 433 (1861)	Lithiophilite and other manganese phosphates. (Reddingite.) Phosphoferrite with triploidite, ludlamite, and vivianite in pegmatite.	pp. 727–29
Landesite			A hydrated phosphate of trivalent Fe and divalent Mn of uncertain formula. Small amounts of Ca and Mg apparently substitute for Mn. $Fe_2Mn_{16}(PO_4)_{16}\ 27\ H_2O$(?).		Found with rhodochrosite, eosphorite, fairfieldite as an alteration product of reddingite in a granite pegmatite	pp. 729–30
Stewartite		Probably triclinic	A hydrated phosphate of manganese.		With palaite and hureaulite as an alteration product of lithiophilite.	p. 730
Salmonsite		Probably orthorhombic.	A hydrated phosphate of trivalent Fe and divalent Mn. $Mn_9Fe_2(PO_4)_8\ 14\ H_2O$ (?).		Alteration product of hureaulite in pegmatites	p. 731
Anapaite	$[Ca_2Fe(PO_4)_2 \cdot 4\,H_2O]_1$	Triclinic, pinacoidal-Ī. Space group $P\bar{1}$.	A hydrated phosphate of calcium and divalent iron. Easily soluble in HCl and HNO_3.			pp. 731–32
Messelite			Anapaite altered in part to collinsite. Not a separate mineral. Composition is near $Ca_2Fe(PO_4)_2\ 2.5H_2O$.			p. 732
Parahopeite	$[Zn_3(PO_4)_2 \cdot 4\,H_2O]_1$	Triclinic; pinacoidal-Ī. Space group $P\bar{1}$.	Dimorphous with hopeite. On heating no water is lost at 139°C. and almost all at 233° C.	By reaction of hot solutions of zinc chloride and sodium ammonium phosphate.	Found with hemimorphite, tarbuttite, pyromorphite, limonite, hopeite, and spencerite.	pp. 733–34

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana Vol. II
Hopeite	$[Zn_3(PO_4)_2 \cdot 4\ H_2O]_4$	Orthorhombic; dipyramidal Space group *Pnma*	Dimorphous with parahopeite. On heating, about half of the water is lost at temperatures up to about 135°C. and the remainder at about 240°C. Easily soluble in dilute HCl	Obtained in crystals by reaction of phosphate solutions with zinc sulfate solution, or from a solution of zinc phosphate in acitic acid. See Spencer, *Mineralog Mag*, **15**, 1 (1908) and Eberly, Gross, and Crowell, *J. Am. Chem Soc* **42**, 1433 (1920)	Hemimorphite, tarbuttite, smithsonite, vanadinite, spencerite	pp 734–37
Hibbenite	$Zn_7(PO_4)_4(OH)_2$ $7\ H_2O$	Orthorhombic, similar to hopeite	Hydrated basic zinc phosphate Part of the water is lost at ordinary conditions and part is retained to red heat The status of hibbenite is uncertain, and the existing data may have been obtained on a mixture of hopeite and spencerite		Spencerite, salmoite hemimorphite.	pp 737–38
Phosphophyllite	$[Zn_2(Fe, Mn)(PO_4)_2$ $4\ H_2O]_2$	Monoclinic; prismatic Space group $P2_1/c$	Soluble in acids		Derived from sphalerite and iron-manganese phosphates in pegmatite.	pp 738–39
Vivianite	$[Fe_3(PO_4)_2\ 8\ H_2O]_2$	Monoclinic; prismatic Space group $C2/m$	Vivianite usually contains more or less ferric iron due to oxidation. The oxidation can extend over a wide range without appar-	Obtained as colorless crystals by heating precipitated ferrous phosphate in a solution of sodium phosphate, by standing a solution of	Weathering product of primary iron-manganese phosphates in pegmatites	pp 742–46

			ent change in crystal structure but with accompanying variation in color and optical properties. The mechanism of the oxidation is not established but may involve a concomitant conversion of (H_2O) to (OH) and H of composition. Easily soluble in acids.	ferrous ammonium phosphate in hydrofluoric acid, and in other ways		
Bobierrite	$[Mg_3(PO_4)_2 \cdot 8\ H_2O]_4$	Monoclinic. Space group $P2_1/c$	Fe'' and Mn substitute for Mg. Easily soluble in acids.	Obtained in crystals by slow precipitation of a $MgSO_4$ solution by a solution of Na_2HPO_4 and $NaHCO_3$. See de Schutten, *Bull. soc. ind., minérale St. Étienne*, **26**, 81 (1903)	With apatite	pp. 753–54
Variscite	$[AlPO_4 \cdot 2\ H_2O]_3$	Orthorhombic; dipyramidal. Space group *Pcab*.	A complete series extends between Fe''' and Al'''. (AsO_4) does not substitute for PO_4 in significant amounts. Most analyses of variscite and strengite are close to the Al or Fe ends of the series. Part of the water is lost below 110°C. and all is driven off at 180°C. in varascite. Soluble in alkalies	Strengite has been obtained as crystals by heating a phosphoric acid solution of ferric chloride in a closed tube at about 185°C Strengite and variscite can be obtained as fine-grained precipitates by addition of NaOH solution to acid solutions containing Fe or Al chlorides and dihydrogen phosphates. See de Schulten, *Compt rend.*, **100**, 15 (1885), and Cole and Jackson, *J. Phys. & Colloid Chem.*, **54**, 128 (1950).	Wavellite, crandallite, metavariscite, microcrystalline apatite, chalcedony, limonite.	pp. 756–61

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Strengite	$[FePO_4\ 2\ H_2O]_8$	Same as variscite	Same as variscite. Strengite only member of series soluble in acid, HCl but not HNO_3	Same as variscite.	Same as variscite	pp. 756–61
Meyerite			Probably ferrian variscite.	Ill-defined substances that may be identical with variscite-strengite or wavellite		pp. 761–62
Callainite			Probably variscite.			
Globosite			Perhaps identical with strengite.			
Fischerite		Orthorhombic; pseudo-hexagonal.	A hydrated basic aluminum phosphate. The only reported analysis does not differ greatly in ratios from those of wavellite.			p. 762
Richmondite		Orthorhombic	A hydrated ferric phosphate. Al substitutes in small amount for Fe''.		With richellite	p. 763
Koninckite						
Metavariscite	$[AlPO_4\ 2\ H_2O]_4$	Monoclinic, prismatic Space group probably $P2_1/m$	Dimorphous with variscite. Fe''' probably can substitute for Al, and a series may extend to metastrengite. Soluble in alkalies.		Variscite	pp. 767–69
Metastrengite	$[FePO_4\ 2\ H_2O]_4$	Monoclinic; prismatic. Space group probably $P2_1/n$.	Dimorphous with strengite. Al apparently substitutes for Fe''' in large amount in some material, and a complete series may extend to metavariscite	Microscopic rose-red monoclinic crystals perhaps identical with metastrengite have been obtained by heating a solution of ferric chloride with phos-	Strengite.	pp. 769–71

			Mn may substitute for Fe. Dissolves completely in HCl, partially in HNO_3.	phoric acid in a closed tube at 180–190°C. See de Schulten, *Compt. rend.*, 100, 1522 (1885).		
Weinschenkite	$[(Y, Er)PO_4 \cdot 2H_2O]_4$	Monoclinic; prismatic Space group $P2/a$ (?)	On heating, loses about $1^1/_2 H_2O$ at roughtly 180°C., the remainder being held to much higher temperatures Soluble in hot acids, insoluble in alkalies	Obtained as a fine-grained precipitate by reaction of yttrium nitrate and tribasic sodium phosphate solutions. See Milton, Murata, and Knechtel, *Am. Mineralogist*, 29, 92 (1944).	Wavellite, crandallite, cacoxenite, beraunite, and dufrenite.	pp. 771–73
Churchite	$(Ce, Ca)PO_4 \cdot 2H_2O$	Monoclinic (?).	A hydrated phosphate of Ce in which Ca replaces Ce to a limited extent	$CePO_4$ $2H_2O$ crystallizes in platy, elongated crystals from the precipitate obtained from a cerium nitrate solution by sodium phosphate See Zambonini, *Bull. soc. ind. minérals St. Étienne*, 38, 206 (1915).		p. 773
Rhabdophane	$(Ce, Y, La, Dy)PO_4 \cdot H_2O$	Tetragonal or hexagonal (?).	A hydrated phosphate of Ce, Y, and rare earth elements. The proportions of the elements occurring with cerium have not been fully determined. The water is largely retained on heating to 200°C. or more. Easily soluble in HCl.			p. 774
Cornetite	$[Cu_3(PO_4)(OH)_3]_4$	Orthorhombic; dipyramidal. Space group *Pbca*.	Material from Katanga, contains a small amount of Co in substitution for Cu. Soluble in cold HCl.		Heterogenite.	pp. 789–91

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Pseudomalachite	$[Cu_5(PO_4)_2(OH)_4 \cdot H_2O\ (?)]_2$	Monoclinic; prismatic, Space group $P2_1/a$.	Reported analyses are somewhat divergent but usually are close to $Cu_5(PO_4)_2(OH)_4\ H_2O$ or $Cu_5(PO_4)_2(OH)_4$ Soluble in acids		Malachite, chrysocolla, tenorite, pyromorphite, chalcedony limonite	pp. 799–801
Andrewsite	$(Cu, Fe'')_2Fe_6'''(PO_4)_4(OH)_{12}$	Orthorhombic (?).	Fe'' substitutes for Cu to about Fe.Cu = 1:1.38 in the only reported analysis and a series may extend to the isostructural species haubmanite			p 802
Lacroixite		Probably monoclinic, pseudo-orthorhombic.	A phosphate-fluoride of Na, Ca, and Al of unknown formula. Partly altered material contains a considerable amount of Mn'', which spectrographic examination shows is lacking in the fresh material. Easily soluble in HCl and H_2SO_4.		Ježekite apatite, childrenite, roscherite, and tourmaline in druses in granite	p 783
Morinite		Monoclinic.	A basic phosphate-fluoride of Na, Ca and Al. The reported analysis of the lamellar mineral corresponds to the formula $Na_2Ca_2Al_3H(PO_4)_4F_6\ 8H_2O$ which differs consider-		Wardite, wavellite, and others as an alteration of amblygonite	p. 784

			ably from jezekite. However it may be part of a series based on jeżekite.		
Jeżekite		Monoclinic; prismatic.	A basic phosphate-fluoride of Na, Ca, and Al, probably $Na_4CaAl_2(PO_4)_2(OH)_2F_2O$. Incompletely decomposed by cold aqua regia or H_2SO_4 but dissolves in hot H_2SO_4.	Roscherite.	pp. 784–85
Laubmannite	$Fe_3''Fe_6'''(PO_4)_4(OH)_{12}$	Orthorhombic (?).	Small amounts of Ca and Mn'' substitute for Fe''. In its unoxidized state laubmannite is the ferrous iron analog of andrewsite.	Limonite	p. 803
Herderite **Hydroxyl-herderite**	$[CaBe(PO_4)(F, OH)]_4$ $[CaBe(PO_4)(OH, F)]_4$	Monoclinic; prismatic. Space group $P2/c$.	(OH) and F substitute mutually and a probably complete series extends between herderite and hydroxyl-herderite. Soluble in acids.	Alteration product of beryllonite	pp. 820–22
Amblygonite **Montebrasite** **Natromontebrasite**	$[(Li, Na)Al(PO_4)(F, OH)]_2$ $[(Li, Na)Al(PO_4)(OH, F)]_2$ $[(Na, Li)Al(PO_4)(OH, F)]_2$	Triclinic, pinacoidal. Space group $P\bar{1}$.	Na and Li substitute mutually. F and OH also substitute mutually to form a probably complete series. Most analyses show a slight excess of water and the formula has been written $(Li,Na)_4Al_4(PO_4)_4(F,OH)_4 \cdot H_2O$. Difficultly soluble in hot acids.	Spodumene, lithiophilite-triphylite, apatite, lepidolite, petalite, pollucite and tourmaline.	pp. 823–27

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], well known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Plumbogummite	$PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$	**Hexagonal-*R* (?)**	Analyses do not agree well with the formula, which was taken from analogy to other members of the plumbogummite group which includes the seven minerals immediately following; all show excess water, and some show varying amounts of CO_2.		Pyromorphite, mimetite, marcasite, cerussite, anglesite wulfenite	pp. 831–32
Ferrazite			A hydrated phosphate of Pb, Ba and Al.			pp. 832–33
Gorceixite		Hexagonal-*R*	A hydrated basic phosphate of Ba and Al of uncertain formula Ca and Ce substitute for Ba to some extent Approximate formula is $BaAl_3(PO_4)_2(OH)_5H_2O$			p. 833
Geraesite			A hydrous barium aluminum phosphate more acidic than gorceixite from the fava accompanying diamonds in river sands in Brazil			p 833
Goyazite	$[SrAl_3(PO_4)_2(OH)_5 \cdot H_2O]_3$ in the rhombohedral unit	Hexagonal-*R*; scalenohedral. Space group $R\bar{3}m$	Ba substitutes for Sr and F is present in some material in substitution for (OH) Slowly soluble in acids		Barite, quartz, pyrite	pp. 834–35
Crandallite	$CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$	Hexagonal-*R*	The formula corresponds to the ideal alunite-type structure but analyses show	A substance apparently identical with crandallite-deltaite is formed by the action of	Deltaite, millisite, wardite, lehiite, alunite and small amounts of calcite	pp 835–37

			marked departures. Sr, Ba, and rare earths may substitute for Ca. Fe''' may substitute for Al Some Ca may enter into positions indicated by the formula as Al positions, giving transitions toward deltaite. All analyses show high H_2O and low P_2O_5 indicating substitution of hydroxyl for (PO_4) Difficultly soluble in acids.	solutions containing $Ca(OH)_2$ and NaOH or fragments of variscite See Larsen, *Am. Mineralogist*, **27**, 288 (1942)		
Deltaite	$[Ca(Al_2Ca)(PO_4)_2(OH)_4H_2O]_1$ in the rhombohedral unit	Hexagonal-*R*, ditrigonal; pyramidal Space group *R*3*m*	Isostructural with crandallite and forms at least a partial series toward that species.		Crandallite	pp 837–38
Florencite	$CeAl_3(PO_4)_2(OH)_6$	Hexagonal-*R*; scalenonhedral	Some Ca and Y may substitute for the Ce earths. The distribution of the several rare earths in florencite has not been fully determined. F is probably present in some material Partially soluble in HCl		Cinnabar monazite xenotime	pp. 838–39
Brasilianite	$[NaAl_3(PO_4)_2(OH)_4]_2$	Monoclinic, prismatic Space group $P2_1/n$	F is lacking in significant amounts. Slowly decomposed by HF or hot H_2SO_4		Muscovite, albite, apatite and tourmaline.	pp 841–43
Griphite	$[(Na, Ca, Fe, Al)_6Mn_4(PO_4)_8(OH,F)_4]_4$	Crystal structure similar to that of garnet	Easily soluble in dilute HCl or HNO_3.		Pegmatites	pp. 843–44

(*continued*)

Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Attacolite			An analysis gave amounts which corresponds roughly to the formula $(Ca, Mn)_3Al_4(PO_4)_4(OH)_6$. Evidence of species validity lacking.		Rarely with berlinite and lazulite	p. 845
Cirrolite			Analysis gave the figures which approximate to the formula $Ca_2Al_2(PO_4)_2(OH)_2$. Slowly decomposed by HCl.			p. 845
Wagnerite	$[Mg_2(PO_4)F]_{16}$	Monoclinic; prismatic Space group $P2_1/a$.	Ca and Fe''' substitute in part for Mg. Highly calcium material has been reported and is due perhaps to alteration Soluble in acids.	Wagnerite and the corresponding calcium compounds, together with the chloride and bromide analogs thereof have been obtained by fusion of the metal halide with ammonium phosphate or the corresponding metal phosphate. The reported Ba and Sr. Analogs of wagnerite have not been verified.	Ferroan magnesite, lazulite, and chlorite.	pp. 845–48
Spodiosite		Orthorhombic (?).	A calcium phosphate-fluoride of uncertain formula, perhaps $Ca_2(PO_4)F$ Soluble in acids		Serpentine, chondrodite, magnetite, and calcite	p. 848

Triphite	$[(Fe'', Mn'')_3(PO_4)\text{-}F]_8$	Monoclinic; prismatic Space group $I2/m$	(OH) substitutes in small part for F, but the limit is uncertain because of the probable presence of nonessential water due to alteration. Fe and Mn substitute mutually over a range of at least Fe:Mn = 1:35 to Fe:Mn = 2.2:1. Mg substitutes for (Fe, Mn, Ca) up to at least Mg:(Fe, Mn, Ca) = 1:2.36 and Ca substitutes for (Fe, Mn) up to Ca:(Fe, Mn) = 1:8.7. Triphite is not isostructural with triploidite-wolfeite. Soluble in acid.	An artificial compound of the composition has been reported by Deville and Caron, *Compt. rend.*. **47**, 985 (1858); *Ann. chim. et. phys.* **67**, 154 (1863).	Triploidite-wofeite, triphylite-lithiophilite, apatite, tourmaline.	pp 849–52
Triploidite Wolfeite	$[(Mn'', Fe'')_3(PO_4)\text{-}(OH)]_{16}$ $[(Fe'', Mn'')_3(PO_4)\text{-}(OH)]_{16}$	Monoclinic; prismatic. Space group $P2_1/a$.	Triploidite and wolfeite form a probably complete series by substitution of Mn'' ande Fe'' Isostructural with sarkinite but evidence is lacking of a series between them. The Fe_2O_3 reported in some analysis is due to partial oxidation of FeO. F does not substitute in significant amounts for (OH) and triplite is not isostructural with wolfeite. Soluble in acids.		Triplite, lithiophilite, and triphylite.	pp 853–55

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Sarcopside		Probably monoclinic	A phosphate-fluoride of uncertain formula, probably $(Fe'', Mn'', Ca)_7(PO_4)_4F_2$ The trivalent Fe reported in the analyses is due probably to partial oxidation.		Pegmatite.	pp. 858–59
Libethenite	$[Cu_2(PO_4)(OH)]_4$	Orthorhombic, dipyramidal. Space group *Pnnm*	A partial series extends between olivenite and libethenite by mutual substitution of As and P, and a partial series extends from adamite toward olivenite by substitution of Cu for Zn Easily soluble in acid and ammonia	Formed as crystals by heating precipitated cupric phosphate with water and preferably excess phosphoric acid in a closed tube at temperatures up to about 200°C. See Friedel and Sarasin, *Bull. soc. ind minérale St Étienne*, **2**, 157 (1879); and De bray, *Compt rend* **52**, 44 (1861)	Malachite, azurite limonite, and pyromorphite.	pp. 862–64
Frondelite	$[(Mn'', Fe'')Fe_4'''(PO_4)_3(OH)_5]_4$	Orthorhombic. Space group probably $B22_12$ or $B22_12$	Fe'', and Mn'' substitute mutually and a probably complete series extends between the Mn and Fe end-members. Small amounts of Mg and Ca substitute for (Mn'', Fe'') and Al and perhaps Mn''' substitutes for Fe'''. The mate-		Vivianite, strengite metastrengite, heterosite, and goethite.	pp. 867–69
Rockbridgeite	$[(Fe'', Mn'')Fe_4'''(PO_4)_3(OH)_5]_4$					

			rial as found is usually more or less oxidized by conversion of Fe'' to Fe''' Soluble in HCl but not in H_2SO_4 or HNO_3		
Tarbuttite	$[Zn_2(PO_4)(OH)]_3$	Triclinic, pinacoidal Space group *P*1		Pyromorphite, hopeite, descloizite, vanadinite hemimorphite, cerussite, smithsonite, limonite.	pp 869–71
Augelite	$[Al_2(PO_4)(OH)_3]_4$	Monoclinic, prismatic Space group *C*2/*m*.	Slowly soluble in hot conc. HCl.	Bournonite and pyrite	pp. 871–73
Dufrenite		Probably monoclinic, pseudoorthorhombic	A hydrated basic phosphate of both divalent and trivalent Fe Formula uncertain probably $Fe''Fe_4'''(PO_4)_3(OH)_5\ 2\ H_2O$. Small amounts of Ca and Cu substitute for Fe''. Al substitutes for Fe''' in some material A dufrenite-like mineral containing much Mn'' in place of Fe'' also has been analyzed. Soluble in dilute acids.	Limonite	pp. 873–75
Dewindtite	$Pb_2(UO_2)_5(PO_4)_4(OH)_4 \cdot 10H_2O$	Orthorhombic	H_2O is largely or entirely lost below 300°C. Soluble in acids.	Torbernite	p. 875
Phosphuranylite		Tetragonal or pseudotetragonal.	A hydrated phosphate of Ca and U of uncertain formula. It appears to be related structurally to dewindtite. Easily soluble in acids.	Autunite and less commonly, uranophane, β-uranophane, hydrated uranium oxides, and opal.	p. 876

(*continued*)

Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Fluorapatite Chlorapatite Hydroxylapatite Carbonate-apatite	$[Ca_5(PO_4)_3(F, Cl, OH)]_2$	Hexagonal; hexagonal-dipyramidal. Space group $C6_3/m$	Fluorapatite, chlorapatite and hydroxylapatite conform to the formula $Ca_5(PO_4)_3(F,Cl,OH)$. Here F, Cl, and OH substitute mutually to form complete series to the essentially pure end-members CO_2 is sometimes found in small amounts as an essential constituent, giving rise to carbonation varieties (see ch. 9). Rare earths, principally Ce, are frequently present in substitution for Ca. Sr sometimes substitutes for Ca. Mg occurs rarely and only in very small amounts, in apatite. Alkalies are present only in traces in ordinary apatite. (SiO_4) and (SO_4) occur in apatite in substitution for (PO_4). (AsO_4) can substitute for (PO_4) and a series probably extends to svabite; As usually is absent. Small amounts of Al, Cr''', Cr^6, and Fe''' appar-	Fluorapatite and chlorapatite have been obtained in crystals by fusion of $Ca_3(PO_4)_2$ or of hydroxylapatite with CaF_2 or $CaCl_2$; also chlorapatite by heating $CaCl_2$, $(NH_4)_2H(PO_4)$, and NH_4Cl in a closed tube, by fusion of $Ca_3(PO_4)_2$ with a large excess of NaCl, by heating $Ca_3(PO_4)_2$ with NaCl and H_2O in a closed tube at 250°C., and in other ways. Hydroxylapatite is afforded by precipitation of solutions of calcium salts by ammoniacal solutions of phosphates, the precipitate may contain excess adsorbed Ca or (PO_4). Also formed by prolonged treatment of $Ca_3(PO_4)_2$ or $CaHPO_4$ in hot water; by heating $4CaO \cdot P_2O_5$ at about 1100°C. in the presence of water vapor or by boiling in water.	Sphene, zircon, pyroxene, amphibole spinel, vesuvianite, phlogopite (for apatite). Rutile, ilmenite, sphene, magnetite pyrrhotite, hornblende, and wernerite (for chlorapatite). Sphene (for hydroxylapatite).	pp. 878–89

			ently can enter apatite in solid solution.			
Pyromorphite Mimetite	$[Pb_3(AsO_4, PO_4)_2Cl]_2$	Hexagonal; hexagonal-dipyramidal. Space group $C6_3/m$.	P and As substitute mutually and a complete series extends between the essentially pure end-members. Ca frequently substitutes for Pb. A complete series apparently does not extend in natural material between calcian varieties of pyromorphite, mimetite, and chlorapatite. F and (OH) apparently substitute for Cl in pyromorphite-mimetite only in trace amounts. Fe'' has been reported in amounts up to about 1 wt-% FeO. Cr is sometimes present in very small amounts V is present in substitution for (As,P). Vanadinite forms a series toward mimetite up to about V:As = 1:1 and a very limited series toward pyromorphite. Rare earths, Sr, Ba, and Mn have been reported in trace amounts. CO_2 is sometimes present in traces. Soluble in HNO_3 and KOH. Pyromorphite is slightly soluble in carbonated water.	Obtained as large crystals by cooling a melt of lead phosphate or arsenate with excess lead chloride. By heating these reagents with water vapor in a closed tube at lower temperatures, or by heating ammonium arsenate or phosphate with lead chloride and water in a closed tube. Mimetite has been obtained in crystals by heating $PbHAsO_4$ in alkali chloride solution or by treating a solution of $PbHAsO_4$ in HCl with lead acetate. Pyromorphite is formed when $PbCl_2$ solution is added to a weak HCl solution containing suspended $Ca_3(PO_4)_2$. The F and I analogs of pyromorphite also have been reported synthesized. See McDonnell and Smith, *Am. J. Sci.*, **42**, 139 (1916); and Jolibois and Chaudron, *Compt. rend.*, **192**, 1650 (1931).	Cerussite and limonite principally. Also smithsonite, hemimorphite, anglesite, malachite, leadhillite, caledonite, vanadinite, wulfenite, descloizite, mottramite, bayldonite.	pp. 889–95

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Svabite	$(Ca, Pb)_5(AsO_4, PO_4)_3(F, Cl, OH)$	Hexagonal; hexagonal-dipyramidal.	Essentially a fluoride-arsenate of Ca. P substitutes for As up to at least P:As = 1.2. Pb substitutes for Ca and both Mg and Mn'' are sometimes also present in minor amounts. Small amounts of both Cl and (OH) substitute for F. With increase of P, svabite forms a series toward fluorapatite and with increase of Pb and Cl a series toward hedyphane and mimetite. Soluble in dilute acids.		Schefferite, garnet, brandite, and sarkinite	pp. 899–900
Dehrnite	$(Ca, Na, K)_5(PO_4, CO_3)_3(OH)$	Hexagonal; isostructural with apatite	The name dehrnite is applied to members of the apatite group that contain significant amounts of alkalies in substitution for Ca, with Na > K. Valence compensation for the substitution of Na, K for Ca presumably is effected by the coupled substitution of C for P or of OH for O Soluble in acids		Crandallite, wardite, deltaite, lehiite, montgomeryite, gordonite, millisite, lewistonite.	pp 902–03

Lewistonite	$(Ca, K, Na)_5(PO_4)_3$-OH	Hexagonal, isostructural with apatite.	The name is applied to members of the apatite group that contain significant amounts of alkalies in substitution for Ca, with K > Na. The mechanism of the valence compensation may involve the coupled substitution of Al for Ca or of OH for O.	Dehrnite, deltaite, crandallite	pp. 903–04
Fermorite		Hexagonal; hexagonal-dipyramidal. Space group $C6_3/m$	An apatite-type phosphate-arsenate of Ca and Sr. F determination probably low. Soluble in acids Formula probably $(Ca,Sr)_5(PO_4,AsO_4)_3(F,OH)$	Braunite, hollandite, and pyrolusite	p. 904
Wilkeite		Hexagonal; hexagonal-dipyramidal; isostructural with apatite. Space group $C6_3/m$.	An apatite-like calcium sulfate-silicate-phosphate. Formula essentially $Ca_5(SO_4,SiO_4,PO_4)_3OH$ Wilkeite apparently is an intermediate member of a series extending from apatite to ellestadite. Easily soluble in HCl or HNO_3.	Diopside, vesuvianite, garnet, crestmoreite, blue calcite	p. 905
Ellestadite		Hexagonal; hexagonal-dipyramidal; isostructural with apatite. Space group $C6_3/m$.	Apparently a member of a series extending through wilkeite to apatite. Formula essentially $Ca_5(SiO_4,SO_4,PO_4,CO_3)_3(Cl,F,OH)$. An apatite-like calcium sulfate-silicate, containing (SO_4) and (SiO_4) in place of PO_4.	Wollastonite, vesuvianite, diopside, okenite, wilkeite, blue calcite.	p. 906

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Tavistockite		Orthorhombic.	A basic phosphate of Ca and Al, $CaAl_2(PO_4)_2(OH)_2$. Material from Katanga is a magnesian variety (by qual. test). Soluble with difficulty in acids		Quartz, childrenite, pyrite, and chalcopyrite.	pp. 906–07
Lazulite **Scorzalite**	$[(Mg, Fe'')Al_2(PO_4)_2(OH)_2]_2$	Monoclinic; prismatic. Space group $P2_1/n$.	A probably complete isomorphous series extends between Fe'' and Mg. Material high in Fe'' is relatively rare Fe''', presumably in substitution for Al, is often present in amounts less than 1 wt.-% Fe_2O_3. The SiO_2 and CaO frequently reported in analyses are ascribed to admixture, and the validity of a reported highly calcian variety is very doubtful Slowly soluble in hot acids		Quartz, rutile, corundum, pyrophyllite, cyanite, andalusite, sillimanite, dumortierite, garnet, muscovite	pp. 908–11
Souzalite	$(Mg, Fe'')_3(Al, Fe''')_4(PO_4)_4(OH)_6 \cdot 2\ H_2O$	Probably monoclinic.	Fe''' substitutes for Al, Fe'' substitutes for Mg. Difficultly soluble in HCl		Alteration product of scorzalite	p. 912
Parsonsite	$Pb_2(UO_2)(PO_4)_2 \cdot 2\ H_2O$	Monoclinic	A hydrated phosphate of lead and uranium The water content is uncertain and probably varies with atmospheric		Torbernite, kasolite, and dewindtite	p. 914

			conditions. Soluble in acids.		
Borickite			Approximate composition $CaFe_5(PO_4)_2(OH)_{11}\ 3\ H_2O$.	In gossan	pp. 915–16
Veszelyite	$[(Cu, Zn)_3(PO_4)(OH)_3\ 2\ H_2O]_4$	Monoclinic, prismatic Space group $P2_1/a$.	Zn and Cu substitute mutually. (AsO_4) substitutes, for (PO_4). The water is entirely lost below red heat. Soluble in acids	Associated with secondary copper minerals.	pp. 916–18
Tsumebite	$Pb_2Cu(PO_4)(OH)_3\ 3\ H_2O$	Monoclinic	A hydrated basic phosphate of lead and copper. Easily soluble in HCl and slowly in HNO_3.	Smithsonite, cerussite, and azurite.	pp. 918–19
Evansite	$Al_3(PO_4)(OH)_6\ 6\ H_2O$		About half of the water is lost at 110°C. and most of the remainder below 300°C. The Fe‴ reported in some analyses presumably substitutes for Al if not due to admixture. Easily soluble in acids.	Limonite, allophane, variscite	p. 923
Rosiérésite			A hydrous phosphate of Al with lead and copper. Needs verification.		p. 924
Renardite	$Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7\ H_2O$	Orthorhombic.	A hydrated basic phosphate of lead and uranium. Soluble in acids.	Dewindtite, dumontite, and torbernite.	p. 928
Dumontite	$Pb_2(UO_2)_3(PO_4)_2(OH)_4 \cdot 3\ H_2O$	Orthorhombic.	A hydrated basic phosphate of lead and uranium. The water is largely or entirely lost below 300°C. Soluble in acids.	Torbernite	pp. 928–29

(continued)

Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Tagilite	$Cu_2(PO_4)(OH)\cdot H_2O$	Orthorhombic (?).	A hydrated basic copper phosphate. Easily soluble in acids and ammonia.		Libethenite, pseudomalachite.	p. 931
Spencerite	$Zn_4(PO_4)_2(OH)_2$ $3\ H_2O$	Monoclinic; prismatic.	A hydrated basic zinc phosphate On heating, $3\ H_2O$ are lost below 140°C. and the remainder is lost only at about 500°C. Readily soluble in acids.		Hemimorphite, hopeite, salmoite.	pp. 931–33
Salmoite			Probably a basic zinc phosphate.		Spencerite, hopeite	p. 933
Isoclasite	$Ca_2(PO_4)(OH)$ $2\ H_2O$ $2\ H_2O$	Monoclinic	A basic hydrated calcium phosphate. Easily soluble in acids		Chalcedony and dolomite	pp. 933–34
Delvauxite			A name given originally to an ill-defined hydrous ferric phosphate, approximately $Fe_4(PO_4)_2(OH)_6\ nH_2O$		Picite	pp. 935–36
Leucophosphite			Formula approximately $K_2(Fe,Al)_7(PO_4)_4$-$(OH)_{11}\ 6\ H_2O$. Apparently formed by the action of solutions derived from bird guano upon serpentine		Variscite, chalcedony, and opal	p. 936

Childrenite Eosphorite	$[(Fe'', Mn)Al(PO_4)(OH)_2 \cdot H_2O]_3$	Orthorhombic; dipyramidal. Space group *Bba*2.	Fe'' and Mn substitute mutually and a complete series probably extends between the two species. Small amounts of Ca and Mg substitute for (Fe,Mn) in some analyses. The Fe''' reported in some analyses is apparently due to oxidation of Fe''. Soluble in acids.	Childrenite associated with siderite, quartz, pyrite, and apatite. Eosphorite associated with rhodochrosite, lithiophilite, triploidite, dickinsonite.	pp. 936–39
Davisonite		Hexagonal (?)	Perhaps $Ca_2Al(PO_4)_2(OH)_3 \cdot H_2O$. Alkalies, not determined in the single analysis of the material, may be present in small amounts as essential constituents.	Crandallite and deltaite	pp. 939–40
Wardite	$[NaCaAl_3(PO_4)_2(OH)_4 \cdot 6H_2O]$	Tetragonal (pyramidal-4(?)). Space group *P*4 or *P*4$_2$.	Appears to be related structurally to millisite. Difficultly but completely soluble in acids.	Millisite and crandallite.	pp. 940–41
Millisite	$(Na, K)CaAl_6(PO_4)_4(OH)_9 \cdot 3\ H_2O$	Probably tetragonal.	Apparently isostructural with wardite and is related simply in composition to that species.	Green wardite.	pp. 941–42
Lehiite		Anisotropic	A hydrated basic phosphate of Na, K, Ca, and Al of in certain formula perhaps $(Na, K)_2Ca_5Al_5(PO_4)_5(OH)_{12} \cdot 6\ H_2O$	Wardite, millisite, crandallite, and occasionally gordonite.	pp. 942–43
Sampleite	$[NaCaCu_5(PO_4)_4Cl \cdot 5\ H_2O]_3$	Orthorhombic; dipyramidal.	Easily soluble in acids	Gypsum, atacamite, libethenite, jarosite, and limonite.	pp. 945–46

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Turquois Chalcosiderite	$[Cu(Al,Fe)_6(PO_4)_4(OH)_8 \cdot 4\ H_2O]_1$	Triclinic; pinacoidal. Space group *PI*.	Probably a complete series between the two is formed by mutual substitution of Fe''' and Al, although most analyses are very close to the Al end of the series. Analyses of turquois usually show somewhat more water than required by the above formula. Soluble with difficulty in HCl.	Obtained by reaction of malachite, hydrous aluminum oxide and phosphoric acid at 100°C. Imitation turquois has been made by compressing or melting together precipitated aluminum phosphate and copper phosphate, also by staining chalcedony or other materials, and as a glass. See Hoffmann, *Fortschr. Mineral., Kryst Petrog.*, 12, 45 (1927); and Mayer, *Chem. Erde*, 9, 311 (1935).	Turquois with limonite, chalcendony and kaolin; also with wavellite. Chalcosiderite with dufrenite, andrewsite, and goethite; also with pharmacosiderite.	pp. 946–51
Harborite		Anisotropic.	Approximate formula $Al_3(PO_4)_2(OH)_3 \cdot 3\ H_2O$.		Dufrenite.	p. 951
Henwoodite			A hydrated basic phosphate of Cu and Al of uncertain formula. Soluble with difficulty in warm HNO_3.		Limonite and chalcosiderite.	p. 951
Ludlamite	$[(Fe'',Mg,Mn)_3(PO_4)_2 \cdot 4\ H_2O]_2$	Monoclinic; prismatic. Space group $P2_1/a$.	Mg and Mn'' substitute in small amount for Fe'' Soluble in acids		Phosphoferrite, triploidite, triplite, triphylite, apatite. Also with fairfieldite, vivianite, siderite, whitlockite as an alteration of triphylite.	pp 952–53

Euguëite		Monoclinic (?)	A hydrous phosphate of ferric iron with minor Ca and Al. Approximate formula $CaFe_{14}(PO_4)_{10}(OH)_{34}$ 21 H_2O Soluble in cold HCl.	Trona and thenardite	p. 955
Mitridatite		Colloidal, perhaps noncrystalline	Essentially a basic phosphate of Ca and Fe containing much water, in part doubtless nonessential. The CO_2 reported apparently is due to admixed calcite and the SO_3 to gypsum or possibly a sulfate-phosphate. Apparent formula $Ca_2Fe_2(PO_4)_2(OH)_2$ n H_2O. Soluble in hot acids.	A metacolloid found in oolitic sedimentary iron cores. In part formed by the alteration of anapaite and vivianite.	pp. 955–56
Richellite			A basic hydrous phosphate of Ca and Fe of uncertain formula, perhaps $Ca_3Fe_{16}(PO_4)_8(OH)_{12}$ n H_2O. Readily soluble in acids.	Halloysite, allophane, koninckite.	pp. 956–57
Englishite	$K_2Ca_4Al_8(PO_4)_8(OH)_{16}\cdot 9\ H_2O$	Probably monoclinic.	A hydrated basic phosphate of K, Ca, and Al of uncertain formula, perhaps $K_2Ca_4Al_8(PO_4)_8(OH)_{16}$ 9 H_2O.	Montgomeryite, wardite, millisite, and crandallite in variscite.	pp. 957–58
Beraunite		Monoclinic.	A hydrated basic phosphate of both ferrous and ferric iron of uncertain formula, perhaps $Fe''Fe_6'''(PO_4)_8(OH)_8\cdot 3\ H_2O$. The mineral as ordinarily found is completely oxidised and the composition then is very close to $Fe_2'''(PO_4)_2(OH)_2\cdot 2\text{–}3\ H_2O$.	Vivianite, dufrenite, rockbridgeite, strengite, cacoxenite, wavellite, limonite. Alteration of triphylite; also of vivianite.	pp. 959–60

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Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Coeruleolactite		Perhaps noncrystalline.	A hydrated basic phosphate of Al of uncertain formula, perhaps $Al_2(PO_4)_2(OH)_3 \cdot 4\ H_2O$. The CaO and CuO reported may be essential constituents. Soluble in acids and alkalies.		Limonite, wavellite.	p. 961
Wavellite	$[Al_3(PO_4)_2(OH)_3 \cdot 5\ H_2O]_4$	Orthorhombic. Space group *Pcmn*.	F often substitutes for OH in small amounts Very small amounts of Fe''' substitute for Al. Fe'', Ca, Mg, and Cr''' apparently also may be minor essential constituents. The water is largely lost below 200° C Easily soluble in acids and alkalies		Limonite, amblygonite, apatite, vauxite, paravauxite, marcasite.	pp. 962–64
Zepharovichite			Probably a mixture consisting principally of microcrystalline wavellite.		Cacoxenite, limonite, strengite, picite	p.964
Sterrettite	$[Al_8(PO_4)_4(OH)_6 \cdot 5\ H_2O]_2$	Orthorhombic; disphenoidal. Space group $P2_12_12_1$.	Almost insoluble in hot acids		Wardite in porous masses of crandallite formed by the alteration of variscite nodules	pp. 965–66

Bermanite		Orthorhombic; dipyramidal.	Essentially a hydrated basic phosphate of divalent and trivalent Mn. Small amounts of Fe''' substitute for Mn''' and of Mg, Ca, Na, for Mn'' Only available analysis affords (Mn, Mg, Ca,-Na)$_5$(Mn, Fe)$_3$(PO$_4$)$_3$-(OH)$_{10}$ 15 H$_2$O. Soluble in nitric acid.	Triplite.	pp. 967–68
Roscherite	(Ca, Mn, Fe)$_2$Al(PO$_4$)$_2$-(OH) 2 H$_2$O	Monoclinic.	Soluble in acids.	Jezekite, lacroixite, childrenite, apatite, and tourmaline.	pp. 969–70
Minyulite		Orthorhombic (?).	Probably KAl$_2$(PO$_4$)$_2$-(OH) 3 5 H$_2$O Soluble in hot conc acids and warm dilute Na-OH.	Dufrenite.	p. 970
Tinticite	Fe$_2$(PO$_4$)$_2$(OH)$_3$ 3.5 H$_2$O	Orthorhombic (?)	Formed by the reaction of phosphatic solutions derived from bat guano with iron from the alteration of pyrite.	Jarosite and limonite.	pp. 970–71
Metavauxite	[FeAl$_2$(PO$_4$)$_2$(OH)$_2$ 8 H$_2$O]$_2$	Monoclinic; prismatic. Space group $P2_1/c$.	Very small amounts of Ca and Mg substitute for Fe.	Vauxite, paravauxite, wavellite.	pp. 971–72
Paravauxite	[FeAl$_2$(PO$_4$)$_2$(OH)$_2$· 8 H$_2$O]$_1$	Triclinic, pinacoidal.	Very small amounts of Ca and Mg substitute for Fe.	Vauxite, metavauxite, wavellite.	pp. 972–73
Vauxite	[FeAl$_2$(PO$_4$)$_2$(OH)$_2$· 7 H$_2$O]$_2$	Triclinic; pinacoidal. Space group $P\bar{1}$.	Very small amounts of Ca and Mg substitute for Fe''.	Wavellite, paravauxite.	pp. 974–75
Gordonite	[MgAl$_2$(PO$_4$)$_2$(OH)$_2$· 8 H$_2$O]$_1$	Triclinic; pinacoidal. Space group $P\bar{1}$.	Isostructural with paravauxite. Soluble in acids.	Variscite. Frequently attached to wardite crusts.	pp. 975–76

(continued)

Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Calcioferrite		Possibly hexagonal	Uncertain formula, possibly $Ca_2Fe_5(PO_4)_4(OH)_3 \cdot 8\ H_2O$ Easily decomposed by HCl			pp. 976–77
Xanthoxenite	$Ca_2Fe(PO_4)_2(OH) \cdot 1.5\ H_2O$	Monoclinic or triclinic	Small amounts of Mn'' and Mg substitute for Ca		Cacoxenite, dufrenite. Whitlockite, eosphorite-childrenite, rockbridgeite.	pp. 977–78
Montgomeryite	$[Ca_4Al_5(PO_4)_6(OH)_5 \cdot 11\ H_2O]_2$	Monoclinic, prismatic Space group $C2/c$			Crandallite, englishite, wardite, millisite, gordonite, and members of the apatite group.	pp. 978–79
Overite	$[Ca_2Al_5(PO_4)_5(OH)_6 \cdot 15\ H_2O]_2$	Orthorhombic, dipyramidal. Space group *Bmam.*	Easily soluble in hot HNO_3		Crandallite, deltaite, and an apatite-like mineral.	pp 979–80
Torbernite	$[Cu(UO_2)_2(PO_4)_2 \cdot 8\text{–}12\ H_2O]_2$	Tetragonal, ditetragonal-dipyramidal Space group $I4'/mmm$	Small amounts of As sometimes substitute for P Pb apparently substitutes for Cu There is no evidence of an isomorphous series with autunite. V, Ba, Mn, and other elements have been found in spectrographic amounts The water content varies with humidity and temperature between 8 and 12 H_2O. 4 H_2O are lost at 55–75°C or at room temperature over a		Autunite and other secondary uranium minerals as an oxidation product of uraninite	pp. 981–84

			desiccant irreversibly (?) forming metatorbernite $Cu(UO_2)_2(PO_4)_2 \cdot 8\ H_2O$. Torbernite is the phase deposited from aqueous solutions up to about 75° C., above this temperature metatorbernite would be formed by direct crystallization Soluble in acids.			
Fritzscheite			Supposedly a Mn, U phosphate of the torbernite group			p. 984
Autunite	$[Ca(UO_2)_2(PO_4)_2 \cdot 10\text{–}12\ H_2O]$	Tetragonal, ditetragonal-dipyramidal Space group $I4/mmm$	Small amounts of Ba and Mg occur in substitution for Ca. Cu apparently does not substitute for Ca to give a series with torbernite V, Pb, and other elements have been reported in spectrographic amounts. The water content apparently varies between 10 and 12 H_2O in autunite. Readily undergoes base exchange, H substitutes for Ca in acid solutions to give an isostructural compound, and Na can substitute for Ca in strong brine solution to give a nonisostructural sodium autunite Soluble in acids.	By reaction of solutions of monocalcium phosphate and uranyl nitrate at low temperatures See Beintema, *Rec trav chim.*, **57**, 155 (1938)	Derived by the alteration of uraninite or other uranium containing minerals.	pp. 984–87

(*continued*)

Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Uranocircite	$Ba(UO_2)_2(PO_4)_2$ $8\ H_2O$	Tetragonal (°).	6 H_2O is lost over H_2SO_4 or by heating below 100°C. Soluble in acids.	Crystals containing 10 H_2O and isostructural with autunite have been prepared by reaction of phosphoric acid with a mixed solution of barium chloride and uranyl nitrate. On heating, a lower hydrate with 2–6 H_2O and isostructural with meta-autunite is formed. See Beintema, *Rec trav chim.*, **57**, 155 (1938).	Parsonite and other secondary uranium minerals	pp. 987–88
Saléeite	$[Mg(UO_2)_2(PO_4)_2$ $10\ H_2O]_2$	Tetragonal; ditetragonal-dipyramidal. Space group $I4/mmm$ if holohedral.	As substitutes for P The Schneeberg material with 10 H_2O is fully hydrated and is isostructural with autunite. The Katanga material with 8 H_2O and biaxial, sectoral crystals, probably is isostructural with the meta-I hydrate of autunite and should then be separated as a species under the name metasaléeite.		Torbernite, dewindtite. Uranophane and zeunerite.	pp. 988–89

Metatorbernite	$[Cu(UO_2)_2(PO_4)_2 8 H_2O]_1$	Tetragonal, ditetragonal-dipyramidal. Space group $P4/nmm$	Stable from solution over about 75°C. On heating, 4 H_2O are lost at about 100°C. forming orthorhombic metatorbernite II, and at about 125°C. an orthorhombic monohydrate is formed which is stable to a higher temperature. Soluble in acids.	Has been obtained by treating artificial autunite in a hot solution of copper chloride See Fairchild, *Am. Mineralogist*, **14**, 265 (1926)		pp. 991–92
Bassetite		Monoclinic (pseudo-orthorhombic).	Analyses are lacking. Apparently a hydrated uranium phosphate containing divalent iron. Loses H_2O in a desiccator at room temperature; the plates then break up into four sectors with the axial planes at right angles and the extinction angle increases to about 20° Soluble in acids.		Uranospathite and torbernite. May be the iron analog of autunite or meta-autunite	pp 994–95

(continued)

Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Cacoxenite	$[Fe_4(PO_4)_3(OH)_3 \cdot 12\ H_2O]_1$	**Hexagonal.**	All the reported analyses are not in good agreement with the formula. In some material small amounts of Al substitute for Fe'''. The green color sometimes observed suggests that the mineral may contain ferrous iron in its original state, analogous to dufrenite. Easily soluble in acids.		Dufrenite, rockbridgeite, beraunite, strengite, wavellite, and limonite.	pp. 997–99
Vashegyite		**Nonisotropic.**	Formula uncertain, perhaps $Al_4(PO_4)_2(OH)_3\ n\ H_2O$. Easily soluble in acids.		Variscite and evansite.	p. 999
Taranakite		**Nonisotropic.**	Formula uncertain, perhaps $K_2Al_6(PO_4)_5(OH)_3\ 18\ H_2O$. The variation between the reported analyses doubtless is due to admixture. Rb is present is spectrographic amounts in material from Minerva Grotto About half of the water is lost at 100°C., and the remainder at red heat.		Product of the reaction of phosphatic solutions derived from bat or seabird guano clays or aluminous rocks	pp. 999–1000

Miriquidite		Rhombohedral.	May be beudantite or corkite.	Pyromorphite.	p. 1002
Corkite		Hexagonal.	Analyses show some substitution of Cu for Pb and some preponderance of (SO_4) over (PO_4). A basic sulfate-phosphate of lead and ferric iron Easily soluble in warm HCl.	Limonite, pyromorphite.	pp. 1002–03
Hinsdalite		Hexagonal.	Sr substitutes for Pb. A basic sulfate-phosphate of lead and aluminum. Practically insoluble in acids but decomposed by fusion in Na_2CO_3.	Quartz, barite, rhodochrosite.	p. 1004
Svanbergite	$[SrAl_3(PO_4)(SO_4)(OH)_6]_1$ in the rhombohedral unit.	Hexagonal-*R*; scalenohedral. Space group $R\bar{3}m$.	Some substitution of Ca for Sr and preponderance of (PO_4) over (SO_4). Slight substitution of Pb for Sr has also been reported. Insoluble in acids.	Kyanite, pyrophyllite. Kaolinite, diaspore.	pp. 1005–06
Woodhouseite	$[CaAl_3(PO)_4(SO_4)(OH)_6]_1$ in the rhombohedral unit	Hexagonal; scalenohedral. Space group $R\bar{3}m$.	Ba substitutes for Ca to a minor extent. Soluble in acids after removal of water by heating.	Topaz, augelite, lazulite, pyrophyllite	pp. 1006–07
Tikhvinite			A basic sulfatephosphate of strontium and aluminum. Close to svanbergite in composition.	Bauxite.	p. 1006
Munkforsite			Allied to svanbergite containing little water. Of doubtful validity.		p. 1006

(continued)

Phosphate Minerals (*continued*)

Mineral name	Chemical formula (Composition of unit cell given in brackets, [], when known)	Crystallographic data	Remarks	Synthesis	Associated minerals	Reference Dana, Vol. II
Munkrudite			Unanalyzed mineral supposedly related to svanbergite. Its validity is most doubtful			0. 1006
Ardealite	$[Ca_2H(PO_4)(SO_4)\cdot 4\ H_2O]_2$	Apparently monoclinic and isostructural with gypsum and brushite.			Brushite and gypsum	pp. 1010–11
Kribergite		Microcrystalline.	Approximate formula $Al_{16}(PO_4)_8(SO_4)_3(OH)_{18}\ 10\ H_2O$		Pyrite.	p. 1011
Diadochite	$Fe_2(PO_4)(SO_4)(OH)\ 5\ H_2O$	Probably triclinic.	The gel types contain a considerable amount of nonessential water above the requirements of this formula Sarmientite apparently is the arsenate analog of diadochite and the two minerals may be isostructural. No sulfate lost on water extraction, easily soluble in acids		Limonite, delvauxite, foucherite, borickite, vashegyite and other hydrous aluminum phosphates, vivianite, pittieite, melanterite.	pp. 1011–13

Kolbeckite		Probably monoclinic	Apparently a hydrated silicate-phosphate of Be, Al, and Ca.	Quartz-wolframite	pp. 1015–16
Vauquelinite		Monoclinic, prismatic-2/*m*.	A chromate-phosphate of Pb and Cu of uncertain formula. Partly soluble in HNO_3.	Crocoite, pyromorphite, and mimetite, also with phoenicochroite.	pp. 650–52
Lueneburgite	$Mg_3B_8(OH)_6(PO_4)_2 \cdot 6\ H_2O$	Probably monoclinic	The water content is uncertain.	Boracite, halite, sylvite, polyhalite, and clay; also guano.	p. 385
Seamanite	$[Mn_3(PO_4)(BO_3) \cdot 3\ H_2O]_4$	Orthorhombic, dipyramidal-2/*m*2/*m*2/*m* Unit cell—P*bnm*	A small amount of (Mg,Ca) substitutes for Mn in the only reported analysis. Soluble in cold dilute acids.	Sussexite, calcite, and manganese oxide.	p. 388–89
Bradleyite	$Na_3Mg(PO_4)(CO_3)$		Slowly decomposed by cold water, Na_2CO_3 going into solution. Easily dissolved in dilute HCl.	Shortite and montmorillonite.	p. 295
Unnamed mineral [see Schaller, *Am Mineralogist*, 213 (1940).]			Composition said to be $2Al_2O_3 \cdot 4\ SO_3 \cdot P_2O_5 \cdot 24\ H_2O$. Soluble in cold water. Does not lose water on heating to 105°C.	Halotrichite, siderotil, and szomolnokite.	p. 634

APPENDIX B

A Collection of Single Bond Energies and Distances (σ-Bonds with Ionic Contributions) with Electronegativity Differences for use in Calculations Concerning Phosphorus Compounds

Bond A–B	Calculated σ-bond distance corrected for ionic shortening (A.)		Bond energy[b] $D_{\sigma,AB} + D_{i,AB}$ (kcal./mole)	Electronegativity difference[b] ($A_A - A_B$)
	S and S[a]	Huggins[b]		
P—H	1 46	1 426	77	0 05
P—C	1.83	1 865	62	0.45
P—Si	2 25	2 25	51	0.25
P—Ge	2 30	2 31	46	0.25
P—N	1.76	1.76	50	0 90
P—P	2 20	2.210	50	0.00
P—As	2 31	2.34	44	0.05
P—O	1.71	1 688	84	1.35
P—S	2.10	2.121	55	0.45
P—Se	2.23	2.27	48	0.40
P—F	1.65	1.612	114	1.75
P—Cl	2.01	2.027	77	1.00
P—Br	2.18	2.191	63	0.80
P—I	2.38	2.420	48	0.50
O—H	0.99	0.963	108	1.30
O—O	1.48	1.474	34	0.00
C—O	1.43	1.435	68	0.90
C—H	1.10	1.118	88	0.40

[a] Calculated according to V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

[b] Calculated according to M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123, 4126 (1953).

*

APPENDIX C

Available Thermodynamic Data on the Compounds of Phosphorus

(These data are taken from the second edition of *Oxidation Potentials* by W. M. Latimer, Prentice-Hall, N. Y., 1952, and are generally in accord with the values in *Circular* 500 of the National Bureau of Standards.)

Class	Compound	Heat of formation, ΔH (kcal./formula wt.)	Free energy of formation, ΔF (s) (kcal./formula wt.)	Standard entropy, S (cal./°C.)
High-temperature phosphorus ions and molecules	P^{2+} (g)	784 51		
	P^{+} (g)	329 81		
	P (g)	75 18	66 71	38 98
	P_2 (g)	33 82	24 60	52 13
	PO (g)	−9 7	—	—
	PN (g)	−20.2	−25.3	50 45
Elemental phosphorus	P_4 (g)	13.12	5 82	66.90
	P_4 (l)	0.601	-	—
	P_4 (c) (α-White P)	0 0	0 0	10 6
	Red P (c)	−4.4	−3 3	(7 0)
	Black P (c)	−10.3	—	—
Metal phosphides	CuP_2 (c)	−28.9		
	Au_3P_3 (c)	−24.1		
	OsP_2 (c)	−40	—	—
Hydrides and halides of phosphorus	PH_3 (g)	2.21	4 36	50 2
	$(P_2H)_n$ (c)	3 4[a]	8 0[a]	(20.)[a]
	PF_3 (g)	—	—	64 13
	PCl_3 (g)	−73.22	−68 42	74 49
	PCl_3 (l)	−81.0	−68.6	—
	PBr_3 (g)	−35.9	−41.2	83.11
	PBr_3 (l)	−47.5	—	—
	PI_3 (c)	−10.9	−8.99	(46)
	P_2I_4 (c)	−19.76	−19.8	(44.2)
	PCl_5 (g)	−95.35	−77.57	84.3
	PCl_5 (c)	−110.7	—	—
	PBr_5 (c)	−66.0	—	—
Phosphonium salts	$(PH_4)Br$ (c)	−29.5	—	—
	$(PH_4)I$ (c)	−15.8	—	—

Class	Compound	Heat of formation, ΔH (kcal./ formula wt.)	Free energy of formation, ΔF (s) (kcal./ formula wt.)	Standard entropy, S (cal./°C.)
Oxyhalides and oxides of phosphorus	$POCl_3$ (g)	−141.5	−130 3	77.59
	$POCl_3$ (l)	−151 0	-	—
	$POBr_3$ (c)	−114 6	—	—
	P_4O_{10} (c)	−720 0	—	-
Hypophosphites	$H_2P(O)(OH)$(c)	−145.5	-	—
	$H_2P(O)(OH)$(aq)	−145 6	−125.1	(38)
	$[H_2P(O)O]^-$ (aq)	—	−122 4	—
Phosphites	$HPO(OH)_2$ (c)	−232.2	—	—
	$HPO_2(OH)_2$ (aq)	−232.2	−204 8	(40.)
	$[HPO(OH)]^-$(aq)		−202 35	(19)
	$[HPO(O)_2]^{2-}$(aq)	−233.8	−194 0	-
	$Na[HPO_2(OH)]$(c)	−289.4	—	-
	$Na_2[HPO_3]$(c)	−338 0	—	—
	$Pb[HPO_3]$ (c)	−234 5	−208 3	(31 9)
Hypophosphates	$H_4P_2O_6$ (aq)	−392	—	-
Orthophosphates	H_3PO_4 (c)	−306 2	—	—
	H_3PO_4 (aq)	−308 2	−274 2	42 1
	$[H_2PO_4]^-$ (aq)	−311 3	−271.3	21 3
	$[HPO_4]^{2-}$ (aq)	−310.4	−261.5	−8.6
	$[PO_4]^{3-}$ (aq)	−306.9	−245 1	−52
	Na_2HPO_4 (c)	−417 4	—	—
	Na_3PO_4 (c)	−460	−430 6	(46 5)
	KH_2PO_4 (c)	−374 9	−339 2	(34 3)
	$Mg_3(PO_4)_2$ (c)	−961 5	−904	(56.8)
	$Mg(NH_4)PO_4$ (c)	—	-390	—
	$Ca(H_2PO_4)_2$ (c)	−744 4	−672	45.3
	$Ca(HPO_4)$ (c)	−435 2	−401 5	21.
	$Ca(HPO_4)\cdot 2\,H_2O$ (c)	−576 0	−514 6	40.
	α-$Ca_3(PO_4)_2$ (c)	−986 2	−929.7	57.6
	β-$Ca_3(PO_4)_2$ (c)	−988 6	−932 0	56.4
	$Sr(HPO_4)$ (c)	−431 3	−399 7	(31.2)
	$Sr_3(PO_4)_2$ (c)	-987.3	−932.1	(70.)
	$Ba_3(PO_4)_2$ (c)	−998 0	−944 4	(85.1)
	$FePO_4$ (c)	-299.6	−272	(22 4)
	$Mn_3(PO_4)_2$ (c)	-771.	−683.	(71.6)
	$Pb_3(PO_4)_2$ (c)	-620.3	−581.4	84.45
Pyrophosphates	$H_4P_2O_7$ (c)	−538.0	—	—
	$H_4P_2O_7$ (aq)	−545.9	-	-
	$[P_2O_7]^{4-}$ (aq)	−543.1	—	—
	$Na_4P_2O_7$ (c)	−760.8	—	-
Metaphosphates	HPO_3 (c)	−228.2	—	—
	HPO_3 (aq)	−234.8	−215.8	(36.)
	$(NaPO_3)_n$ (c)	−288.6[a]	—	—

[a] The value corresponds to $n = 1$.

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