Systematic Inorganic Chemistry

OF THE FIFTH-AND-SIXTH-GROUP NONMETALLIC ELEMENTS

by

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To
WILLIAM C. BRAY
ABLE SCIENTIST, INSPIRING TEACHER

Preface

Inorganic chemistry has undergone a marked transition in the last three decades as it has grown from an almost purely descriptive branch of science to a field in which all of the modern developments of physics and chemistry find application. In this field the quantum theory plays an important role in the establishment of energy states and molecular structures and in the explanation of the periodic law; thermodynamics finds application in the prediction of the degree of completion of chemical reactions at equilibrium; statistical mechanics makes possible the calculation of the thermodynamic properties of substances from atomic and molecular data and deepens our insight into the still unsolved problems of the rates of chemical reactions; finally, the phenomena of natural and artificial radioactivity not only increase our knowledge of the fundamental structure of matter but also, through the use of radio-elements as tracers, greatly extend our understanding of the mechanisms of chemical reactions. From these considerations it is evident that any discussion of a chemical element or compound is complete only when the spectroscopic, structural, thermodynamic, chemical kinetic, and nuclear properties have been considered. In addition to these more modern aspects of the subject, due consideration must be given to the older, humbler, but nevertheless important, chemical facts that one finds in simple experiments with test tubes, beakers, and flasks.

Since the field of inorganic chemistry embraces all of the chemical elements, a complete discussion of the whole subject would require volumes to record. Therefore, the authors have chosen to cover a selected list of chemical topics and to include in the discussion of each enough of both the old and the new chemistry to bring out the most important features of the substances examined.

The subject matter of this book is devoted to the inorganic chemistry of the nonmetallic elements of the fifth and sixth groups of the periodic system. These elements and their compounds, besides being of great practical and theoretical interest in themselves, exhibit, in their properties and reactions, characteristics that are common to many other substances both inorganic and organic. The factual material chosen for presentation has been selected as critically as possible, and the sources are the original literature or the results of the authors' own researches. The quantitative information presented was taken, for the most part, without change directly from original articles describing what appear to be the most reliable investigations available. Since it is not always possible to make a selection of experimental data on a purely objective basis, in doubtful cases some allowance must be made for the opinions of the authors.

But a survey of a field of science from a purely critical point of vie does not satisfy all of the needs of the research man or advanced stud Also needed is material of a stimulating nature that will suggest fields th require further research for their more complete understanding. In the topics presented in this book, the reader will find many problems worthy of the serious attention of research workers in both pure and applied chemistry. Further, the advanced student should gain from the topics discussed a feeling for the present state of knowledge, and an appreciation of what has been accomplished in the past and what may be reasonably expected of the future.

The subject matter considered here, together with such additional topics as the halogens, coordination compounds, the metals, and artificial radioactivity, form the basis of the senior and graduate courses in inorganic chemistry given at the California Institute of Technology. It is required that the students of both classes shall have already received thorough training in undergraduate physics, organic chemistry, and chemical thermodynamics. In some cases—for example, in the use of statistical mechanical methods—the principles and theory, though simple, have not yet been included in the physics and physical chemistry courses, and, consequently, the necessary material must be presented along with the topic best suited to the purpose. In general, the inclusion in the course of such necessary additional material adds spice to the main subject. Both chemistry and physics are currently providing so much that is new in fact and theory that the pedagogical methods of presenting the advanced parts of inorganic chemistry have not, fortunately, been crystallized into a discipline. Accordingly, the instructor using this book either as the main text or for reference is restricted only in that the topical method of approach is clearly indicated. That the research point of view is emphasized should, it is believed, prove advantageous from the teacher's standpoint.

References in the text to the literature are frequent but are not to be regarded as exhaustive or complete; an attempt has been made to give either significant references or ones that will provide the reader with a convenient key to further information. Recent books on more or less specialized subjects, such as those listed in the Bibliography in appendix A, are also referred to as sources of original material. It scarcely needs saying that such books are indispensable as auxiliary texts for courses in advanced inorganic chemistry.

Acknowledgment for assistance in the selection and collection of material is gratefully made to the graduate and undergraduate students of advanced inorganic chemistry at this Institute. Dr. W. V. Claussen kindly assisted at the early stages of the work on the book. Dr. David P. Stevenson generously made many of the thermodynamic calculations for the chapters on phosphorus and sulfur. Invaluable aid came from many scussions with other members of the chemistry division staff; this aid s been especially helpful in the cases of Professors Richard M. Badger, Roscoe G. Dickinson, Howard J. Lucas, Linus Pauling, Richard C. Tolman, and Dr. Verner Shomaker. Deep appreciation for the early help and inspiration of Professors W. C. Bray and A. A. Noyes is gratefully expressed. Mr. and Mrs. John B. Hatcher prepared all of the drawings and figures, and special acknowledgment is due them for their assistance and interest throughout the work. The curves in the text were carefully drawn through accurate plots of the published experimental data; in only two cases were graphs taken directly from the literature. Mrs. Marguerite S. Yost, Dr. D. V. R. Golding, and Max Cayley Yost assisted in many ways in the writing and preparation of the manuscript, in the correction of the proofs, and in the construction of the indexes. We wish also to thank the staff of Prentice-Hall, Inc., and the editor of their chemistry series, Professor W. M. Latimer, for their help and cooperation throughout.

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Horace Russell, Jr.

Pasadena,
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CHAPTER 1

Nitrogen and Its Oxides and Sulfides

Elementary Nitrogen

Preparation

Nitrogen is present as such in the atmosphere to the extent of 78.09% by volume in clean dry air (O_2, 20.95%; A, 0.93%; CO_2, 0.03%; H_2, 0.00005%; Ne, 0.0018%; He, 0.00052%; Kr, 0.0001%; and Xe, 0.000008%). The average chemical composition of dry air is remarkably uniform as regards both its geographical and vertical distribution. Samples taken during balloon flights have failed to show any sign of variations up to about 20 km. Above that level, a minute prevalence of helium is indicated, marking an incipient change from convective mixing to diffusion equilibrium. This gravitational separation according to molecular weights was formerly used as the chief support of the hypothesis that the uppermost stratosphere should be practically pure hydrogen. Modern spectroscopic observations of the light emitted by the Aurora Borealis, extending up to 500 km and more, have refuted this contention [Wildt, *Rev. Mod. Phys.*, **14**, 151 (1942)].

Air is not a satisfactory material for the preparation of very pure nitrogen because the noble gases present, mainly argon, are not easily removed. To prepare pure nitrogen, the following chemical methods may be used. (1) A saturated solution of $NaNO_2$ is allowed to drop slowly into a heated mixture of saturated solutions of ammonium chloride and potassium dichromate; the main reaction is the decomposition of ammonium nitrite (which see). The resulting gas must be further purified by passing through dilute H_2SO_4 (to remove any NH_3), $FeSO_4$ solution (to remove any NO), heated copper, P_2O_5, and finally a trap cooled with liquid air. A further fractional evaporation is also desirable [Kamerlingh Onnes and van Urk, *Comm. Leiden*, **16**, No. 169d (1924)]. (2) Ammonia gas is passed into bromine water, and the resulting gases are passed through suitable absorbents to remove ammonia, bromine, water, and any other impurities. The main reaction involved in this method of preparation is the oxidation of ammonia by bromine, $2NH_3(aq) + 3Br_2 = N_2 + 6HBr(aq)$ [Giauque and Clayton, *J. Am. Chem. Soc.*, **55**, 4875 (1933)]. (3) Sodium (or barium) azide, after purification by recrystallization, is carefully dried at 100° to 150° and then heated in a closed system to 300°. The nitrogen evolved according to the reaction $2NaN_3(s) = 2Na(l) + 3N_2(g)$ is spectroscopically pure. This statement is true if the first gases formed are discarded, since they may contain small quantities of hydrogen if the azide salt is not perfectly dry. This method is ordinarily used for the preparation of comparatively small amounts of nitrogen, the present cost of the azides being somewhat too high to permit their use for the preparation of large quantities of gas.

If great purity is not required, nitrogen, containing argon and small quantities of oxygen, may be obtained by the fractional distillation of liquid air. Any oxygen that remains after the fractionation may be effectively removed by passing the impure nitrogen through a mixture of aqueous ammonia and metallic copper turnings and then through sulfuric acid; the complex ion $Cu(NH_3)_2^+$ is readily oxidized to $Cu(NH_3)_4^{++}$ by oxygen. White phosphorus is also used to remove small amounts of oxygen from nitrogen. The nitrogen furnished in steel cylinders is manufactured by the fractional distillation of liquid air.

Physical properties

The nitrogen molecule is diatomic, N_2. It has been found to be diamagnetic, the specific susceptibility being -0.430×10^{-6} at 20° [Havens, *Phys. Rev.*, **43**, 999 (1933)], and from this fact it may be concluded thalt the nitrogen molecule in its ground state does not have a resultant electronic angular momentum. Both the rotational and vibrationa ene rgy states have been accurately determined from a study of the emission and Raman spectra of the gas. Lines due to the rotation of the molecule have alternating intensities, this phenomenon being shown in a particularly beautiful manner by the pure rotational Raman spectrum [Rasetti, *Phys. Rev.*, **34**, 367 (1929)]; the lines arising from transitions between states with even values of the rotational quantum number J are twice as intense as those for which J is odd; that is, in the gas there are twice as many molecules having J even as there are molecules having J odd. The alternation of intensities shows that the nitrogen nucleus possesses spin properties. For, according to the quantum theory, the ratio of the intensities of the rotational lines for a symmetrical diatomic molecule (at ordinary temperatures) will be $I + 1/I$ where I is the nuclear spin quantum number; accordingly, from $I + 1/I = 2$ we conclude that $I = 1$. That part of the eigenfunction for a diatomic molecule due to *nuclear rotation* about an axis perpendicular to the line joining the two nuclei is symmetrical for J even and antisymmetrical for J odd, with respect to interchange of the nuclei. Experiment shows that nitrogen gas at ordinary temperatures contains twice as many molecules with J even as with J odd. Now, of the $(2I + 1)^2$ possible *nuclear* spin eigenfunctions, it may be readily shown that $I(2I + 1)$ are antisymmetric and $(2I + 1)^2 - I(2I + 1) = (2I + 1)$

$(I + 1)$ are symmetric.[1] Since for nitrogen $I = 1$, there will be six symmetric and three antisymmetric *nuclear spin* functions; that is to say, the ratio of the number of symmetric to antisymmetric nitrogen molecules in the gas will be $6:3 = 2$. It follows from the experimental facts that for J even the molecules are symmetric in the *nuclear spin*, and for J odd antisymmetric; that is, the symmetric *nuclear spin* functions are to be associated with the symmetric (J even) rotational functions. Now, the interchange of two composite nitrogen nuclei is equivalent to the interchange of a number of constituent fundamental particles, protons, neutrons, electrons, and so on. According to the principle that interchange of two fundamental particles must lead to a change in sign of the complete eigenfunction (alternation principle) for the molecule, it follows that the nitrogen nucleus must consist of an even number of fundamental particles, since the combined *rotational-nuclear spin* functions are all symmetric with respect to interchange of the two nuclei. Inasmuch as the atomic number of nitrogen is 7 and the atomic mass number is 14, the nucleus could consist of seven protons and seven neutrons, a total of 14 fundamental particles, but it could not consist of 14 protons and 7 electrons or 14 neutrons and 7 positrons, since these combinations lead to an odd number of fundamental particles in the nucleus. It is remarkable that the results of molecular spectra experiments have led rather directly to information about nuclear structure, and, indeed, the assumption of the existence of neutrons was first made to account for the molecular spectra of nitrogen. The neutron subsequently found in nuclear disintegration experiments has a greater mass than that first postulated to explain the nitrogen molecular spectrum.

The existence of two kinds of nitrogen molecules raises the question whether the rotational heat capacity of the gas will, like that of hydrogen, depend on the temperature in a manner suggesting that the symmetrical and antisymmetrical N_2 molecules change only very slowly into each other. The answer is that in the temperature range for which nitrogen is a gas the rotational heat capacity, $C_{rot.}$, is a constant and equal to R. This is due to the fact that the moment of inertia, I, of the N_2 molecule is relatively large, and consequently the energy levels $\epsilon_{rot.} = J(J + 1)h^2/8\pi^2 I$ are closely spaced.[2] Any variation with temperature would come

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[1] For each nucleus there are $2I + 1$ nuclear eigenfunctions α, β, γ . . . corresponding to the $2I + 1$ orientations that a nucleus with spin I would assume in a magnetic field. For a symmetrical diatomic molecule with the like nuclei A and B, the nuclear eigenfunctions will be of the form $\alpha(A)\alpha(B)$, $\beta(A)\beta(B)$, $\gamma(A)\gamma(B)$, and so forth, $1/\sqrt{2}\,[\alpha(A)\beta(B) + \alpha(B)\beta(A)]$, and so forth, $1/\sqrt{2}\,[\alpha(A)\beta(B) - \alpha(B)\beta(A)]$, and so forth. It is not difficult to determine the number of combinations that will be symmetric and antisymmetric with respect to interchanging the symbols A and B.

[2] When the energy levels are closely spaced, the distribution of molecules among the rotational energy levels approximates the classical Maxwell-Boltzmann distribution for which $C_{rot.} = R$ at all temperatures. Even with closely spaced levels, a low

at the low temperatures at which nitrogen is a solid of very low vapor pressure, namely, in the range 0° to 20°K. The composition of the 2:1 mixture will not, therefore, undergo appreciable change with temperature except possibly at very low temperatures.

The even number of fundamental particles in the nitrogen nucleus and the odd number of extranuclear electrons requires that diatomic nitrogen obey the Bose-Einstein distribution law.

There are two isotopes of nitrogen, namely, N^{14} and N^{15}, and in ordinary nitrogen these are present in the ratio of 346:1 [Murphy and Urey, *Phys. Rev.*, **41,** 141 (1932)]. The heavier isotope has been obtained at greater concentrations than found in nature by a process of fractionation. Organic compounds made from the concentrate are used in biochemical studies, the "heavy nitrogen" serving as a tracer.

The rotational energy states of $N_2(g)$ are given by the empirical formula:

$$\epsilon_{rot.} = [B + \alpha(v + \tfrac{1}{2})]J^2 + [D + \beta(v + \tfrac{1}{2})]J^4$$

$J = 0, 1, 2 \cdots$, the rotational quantum number.
$v = 0, 1, 2 \cdots$, the vibrational quantum number.
$B = 2.003\ \text{cm}^{-1}$, $\alpha = -0.023\ \text{cm}^{-1}$, $D = -5.773 \times 10^{-6}\ \text{cm}^{-1}$, $\beta = 8.61 \times 10^{-8}\ \text{cm}^{-1}$.

These values of B, α, D, and β give $\epsilon_{rot.}$ in cm^{-1}. The vibrational energy states may be calculated from the formula:

$$\begin{aligned} \epsilon_{vib.} &= \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 \\ v &= 0, 1, 2, \cdots \\ \omega_e &= 2359.61\ \text{cm}^{-1} \qquad \omega_e x_e = 14.445\ \text{cm}^{-1} \end{aligned}$$

[See Birge and Hopfield, *Phys. Rev.*, **29,** 212 (1927).]

The N-N internuclear distance of the molecule in the normal state is 1.095 Å [Rasetti, *Phys. Rev.*, **34,** 367 (1929)], and this corresponds to a triple electron-pair bond between the two atoms, namely, :N:::N:. The dissociation energy for the reaction $N_2(g) = 2N(g)$ is 170,275 cal at 0°K, and $\Delta H^\circ_{291} = 171{,}175$ cal [Herzberg, *Molecular Spectra and Molecular Structure,* Prentice-Hall, New York; Bichowsky and Rossini, *Thermochemistry,* Reinhold, New York]. The thermal decomposition of N_2 into N has not been observed in laboratory experiments; the dissociation energies given here were determined spectroscopically.

The general physical properties of nitrogen are presented in the following table. [See Curtis, *Fixed Nitrogen,* Chemical Catalog Co., New York; Baley and Donnan, *J. Chem. Soc.*, **81,** 907 (1902); Giauque and Clayton, *J. Am. Chem. Soc.*, **55,** 4875 (1933).] There are two solid

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temperature can be reached at which the number of molecules in the lowest rotational level is a much larger fraction of the total number than is the case with a gas consisting of classical rotators.

modifications of nitrogen, the low-temperature or α (cubic) form, and the higher-temperature, above 35.61°K, or β (hexagonal) form; nitrogen is colorless in all of its modifications.

TABLE 1
THE PHYSICAL CONSTANTS OF NITROGEN

0°C = 273.1°K

Melting point = 63.14°K ΔH (fusion) = 172.3 cal/mole at m.p.
Boiling point = 77.32°K ΔH (evap.) = 1332.9 cal/mole at b.p.
Transition temp. (α to β) = 35.61°K ΔH (trans.) = 54.71 cal/mole
Vapor pressure of solid (β) $\log_{10} p_{cm} = -381.6/T - 0.0062372T + 7.41105$
Vapor pressure of liquid* $\log_{10} p_{cm} = -339.8/T - 0.0056286T + 6.71057$
Surface tension of liquid $\gamma_T = 11.68(1 - 0.00863T)$ dynes/cm
Density solid (g/cm³) D = 1.0265 at 20.6°K, 0.8792 at 63°K
Density liquid (g/cm³) $D = 1.1604 - 0.00455T$
Weight of one liter N_2(g) at 0° and 760 mm = 1.25046 g
Critical temperature = 126.0°K Critical pressure = 33.5 atm

Heat Capacity, C_P (cal/deg/mole) for Solids and Liquid

	α		β			Liquid		
T(°K)........	15.82	35.05	39.13	55.88	61.41	65.02	70.28	77.74
C_P	3.124	10.84	8.948	10.44	11.07	13.33	13.45	13.64

Entropy, S_T° (cal/deg/mole), of N_2 Gas (Ideal) at 1 atm

T(°K)	$S^\circ_{(\text{Exp.})}$	$S^\circ_{(\text{Spectroscopic})}$
77.32	36.5	36.416
298.1	45.9	45.788

Heat Capacity, C_P, in cal/deg/mole of N_2 Gas (Real) at Various Temperatures and Pressures

(C_P = 6.953 cal/deg/mole for ideal gas at room temperature.)
$C_P = 6.76 + 0.606 \times 10^{-3}T + 0.13 \times 10^{-6} T^2$ for 300–2500° and 1 atm

Press. (atm)............	1	50	100	500	1000
T(°C):					
30..........	6.91	7.41	7.92	9.12	(9.25)
100.................	6.94	7.21	7.48	8.39	(8.6)
600.................	7.13		7.19	7.36	7.46

Viscosity η of N_2 gas in $\text{cm}^{-1}\ \text{g sec}^{-1}$ at about 1 atm

$$\eta = \frac{KT^{3/2}}{C + T}, \quad K = \eta_0 \frac{C + T_0}{T_0^{3/2}}$$

$T_0 = 273.16°\text{K} \qquad K = 137.7 \times 10^{-7} \qquad C = 102.7$
$\eta_{17°} = 1738.2 \pm 0.7 \times 10^{-7}$ [Rigden, *Phil. Mag.*, **25**, 961 (1938).]

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* Keesom and Bijl [*Physica*, **4**, 305 (1937); *Proc. Acad. Sci. Amsterdam*, **40**, 235 (1937)]

Nitrogen does not obey the perfect gas law even at ordinary pressures and temperatures, although the deviations are not great. Thus, if we select volume units such that $PV = 1.0000$ for $P = 1$ atm, then $PV = 1.00011$ at $\frac{2}{3}$ atm and 1.00028 at $\frac{1}{3}$ atm, at ordinary temperatures [Baxter and Starkweather, *Proc. Nat. Acad.*, **12,** 703 (1926)]. For ordinary pressures ($\frac{1}{2}$ to 1 atm) and low temperatures (77–90°K), $PV = nRT(1 - BP)$ with $B = 0.0022 + 19600/T^3$ atm^{-1}. Accordingly, at about 100°K and 1 atm $B \approx 0.02$; that is to say, nitrogen shows a deviation of about 2% from the behavior of a perfect gas. At room temperatures the deviation may also be seen: (1) from the variation of the coefficient of expansion α with pressure in $V = V_0(1 + \alpha t)$, where $\alpha \times 10^{+7} = 36604 + 127P$ for $t = 0°$ to $100°$, and P is in meters of Hg;

TABLE 2
PV VALUES FOR NITROGEN[a]
($PV = 1.0000$ at 1 atm and 0°C)

Pressure (atm)	−100°	0.0°	50°	100°	200°	300°	400°
1.	0.6319	1.0000	1.1835	1.3669	1.7335	2.1000	2.4663
10	.6109	.9962	1.1836	1.3695	1.7398	2 1083	2.4758
50	.5180	.9848	1 1884	1.3849	1.7694	2.1462	2 5189
100....	.4471	.9848	1.2046	1.4121	1.8111	2.1973	2.5751
500		1.3885	1.6171	1.8388	2.2708	2.6774	3 0714
1000...........		2.0641	2.2825	2 4948	2.9212	3.3203	3.7224

[a] In the Beattie-Bridgman equation of state [*Proc. Natl. Acad.*, **16,** 14 (1930); Deming and Shupe, *J. Am. Chem. Soc.*, **52,** 1382 (1930)], $P = RT(1 - \epsilon)(v - B)/v^2 - A/v^2$, $A = A_0(1 - a/v)$, $B = B_0(1 - b/v)$, $\epsilon = C/vT^3$, the constants have, for nitrogen, the values $A_0 = 1.254 \times 10^6$, $a = 18.68$, $B_0 = 46.04$, $b = -25.88$, $C = 61.65 \times 10^6$. The units are pressure in atm, volume in cc/mole, $RT = 22414$ cc/atm/mole at 0°C. For isotherms from 127°K to 373°K, see Kamerlingh Onnes and van Urk [*Comm. Leiden*, **16,** Nos. 169d and 169e (1924–1926)].

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have made a careful redetermination of the vapor pressures of solid (β) and liquid nitrogen. The results may be calculated from an empirical equation whose form is convenient for the evaluation of temperatures from vapor pressure measurements.

$$\text{Liquid, } \frac{1}{T + \Delta T} = -3.20398 \times 10^{-3} \log_{10} p_{\text{cm}} + 1.89532 \times 10^{-2}$$

T(°K)........................	64.37	66.98	70.09	74.12	77.50
ΔT...........	0.025	.053	.073	.055	−.008

$$\text{Solid, } \frac{1}{T + \Delta T} = 2.7748 \times 10^{-3} \log_{10} p_{\text{cm}} + 1.85350 \times 10^{-2}$$

T...........	53.26	55.82	58.10	60.78	63.10
ΔT........................	0.010	.014	−.007	.009	− 003

m.p. = 63.15°K   b.p. = 77.357°K   0°C = 273.144°K

The difference between these boiling and melting points and those given in Table 1 are believed to be due to differences in temperature scale.

and (2) from the ratio $PV(0°, 0 \text{ atm})/PV(0°, 1 \text{ atm}) = 1.00047$. It must be emphasized here that the values of α and of the $(PV)_0/(PV)_1$ ratio are subject to change, since highly accurate values require very pure nitrogen and careful experimentation, and both of these factors are subject to improvements or changes by successive investigators. For example, a recent determination of α [Kinoshita and Oishi, *Phil. Mag.*, **24**, 52 (1937)] for the limit $P = 0$ resulted in the value 36607×10^{-7}, which is slightly higher than that given by the formula above. The reciprocal of 36607×10^{-7} is 273.16, and this is in good accord with 0°C = 273.16°K, the accepted value.

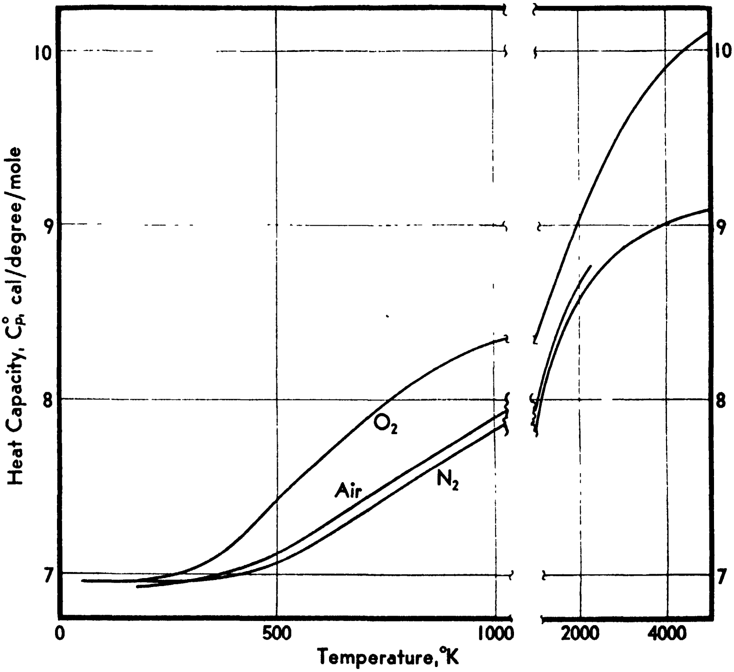


Fig. 1. The Molal Heat Capacity of Air, Nitrogen, and Oxygen in the Ideal Gaseous State.

The gas imperfections shown by nitrogen become greater at higher pressures, and it is in the high-pressure range that important industrial applications are made. For example, in the synthetic ammonia process, pressures as high as 1000 atm are employed. In Table 2 are presented representative PV, T data for gaseous nitrogen.

It is evident on examining the columns of Table 2 that nitrogen deviates appreciably from the behavior of a perfect gas at low temperatures, but that above 0° the deviations are not great at pressures less than 100 atm. If the gas were perfect, the values of PV in any one column of the table would be constant.

Nitrogen was at one time used in gas thermometers for the determination of absolute temperatures on the thermodynamic Kelvin scale. For this purpose it is necessary to know accurately the deviations from the law of ideal gases, namely, $PV = nRT$. Nitrogen is largely replaced now by helium, since the properties of the latter are much closer to those of a perfect gas than are those of any other known substance; moreover, helium does not condense at atmospheric pressure until a temperature of 4.216°K is reached. The limiting value for low pressures of the temperature coefficient of pressure, B, for nitrogen $[P = P_0(1 + Bt)]$, is given variously as 0.0036618, 0.0036606, and 0.0036613, the value depending on the investigator; the corresponding ice-point temperatures $(1/\beta = T_0)$ are 273.09°, 273.20°, and 273.13°K, respectively. The limiting value of the coefficient of expansion α is given as 0.0036604 and 0.0036607, and $T_0 = 1/\alpha = 273.21$ and 273.16°K. The accepted value of T_0 obtained with helium is 273.16°.

Nitrogen is only slightly soluble in water, and the solutions contain no detectable ions containing nitrogen; electrolysis of salt solutions saturated with the gas under pressure does not yield nitrogen compounds. The volumes v_0 of nitrogen, reduced to 0°C and 1 atm, absorbed by one volume of water when the partial pressure of N_2 is one atmosphere, for several temperatures are as follows:

t(°C)...............	0	20	30	50	100
v_0..................	0.02312	.01518	.01319	.01071	.00947

Henry's law is obeyed fairly well by the solutions. The solubilities in NaCl solutions are less than in pure water, but alcohol is capable of dissolving approximately eight times as much at 20° as does water at the same temperature.

Chemical properties

Although nitrogen is unreactive toward most reagents at ordinary temperatures, it is rapidly adsorbed by charcoal in quantities that increase with decreasing temperature of the adsorbent. At liquid-air temperatures, appreciable amounts are adsorbed before the equilibrium pressure rises above 10^{-5} mm Hg, and it is for this reason that charcoal traps cooled with liquid air are sometimes used in high-vacuum work. A common and effective method of freeing helium from nitrogen and other gases takes advantage of the fact that helium is not adsorbed by charcoal at low temperatures nearly so extensively as is nitrogen, the ratio of the amounts for a given sample of charcoal and for about 1 atm pressure being approximately 1:50 at −190° and 1:250 at −48°. Coconut charcoal is a good adsorber for nitrogen, but blood or animal charcoal is superior to it, as the following results of Hempel and Vater [*Z. Electrochem.*, **18**, 724 (1921)] for atmospheric pressure show. In practice coconut charcoal has advantages resulting from its resistance to crushing and powdering. The effect of pressure on the amounts of nitrogen adsorbed by coconut charcoal is also presented in the table [Titoff, *Z. phys. Chem.*, **74**, 641 (1910)]. Charcoals vary considerably, and the results cited are for particular samples.

TABLE 3

ADSORPTION OF NITROGEN BY CHARCOAL

(The volumes v_0 in cc adsorbed have been reduced to 0° and 1 atm.)

Temp. (°C)	20	−78	−185
v_0 per cc of coconut charcoal[a]	15.7	79.2	219.4
v_0 per cc of blood charcoal	21.0	107 4	632.2

[a] Heated at 600°, the optimum activation temperature, before measurements were made. For both charcoals the pressure of N_2 was about 1 atm.

v_0 in cc for 35.662 g Coconut Charcoal, Activated at 550° and Evacuated to 10^{-3} mm Before Measurements Were Made, for Various Equilibrium Pressures

151.5°		0°		−79°	
p_{cm}	v_0	p_{cm}	v_0	p_{cm}	v_0
1.89	1.324	0.43	3.967	0.15	5.169
8.34	5.050	3.93	35.203	1.25	123.690
31.61	18.018	22.94	181.221	14.95	714.126
77.07	41.783	77.46	465 484	38.84	1192.080
				74.06	1551.625

Heat of adsorption, 0° q, = 0.210 cal/cc (NTP) of adsorbed N_2. q is practically independent of the pressure.

To give some notion of the relative behavior of another gas toward the same sample of coconut charcoal, 35.662 g, the values of v_0 for hydrogen for two temperatures and atmospheric pressure may be cited. At 0° and 74.42 cm, $v_0 = 55.477$ cc, and at −79° and 72.16 cm, $v_0 = 193.068$ cc. It is evident that about eight times as much nitrogen as hydrogen is adsorbed by the sample of charcoal at the temperatures considered. This factor increases somewhat with decreasing pressure. v_0 may be represented fairly satisfactorily by the formula $v_0 = CP^{1/n}$, where C is a constant depending on the amount and character of the charcoal, and n is another constant, for a given temperature, with a value near unity ($1/n = 0.976$) for the 151.5° results shown in the table.

The reactions of nitrogen with oxygen at high temperatures and with hydrogen at high pressures in the presence of a catalyst are discussed in detail in a later section.

Nitrogen reacts at more or less elevated temperatures with a number of metals and some compounds. Characteristic is the ability of the heated alkaline earth metals to absorb nitrogen rapidly and readily. On the other hand, the alkali metals, with the exception of lithium, do not react with nitrogen even on strong heating, although stable alkali nitrides prepared by indirect methods are known. The following table presents the compounds formed and the conditions for reaction for a number of metals.

TABLE 4

REACTIONS OF NITROGEN WITH METALS

Metal	Compound Formed	Temp. (°C) Minimum for Reaction	Remarks	$\Delta F^\circ_{298.1}$[b]
Li[a]	Li_3N	Slow at room temp., rapid at 250°.	O_2 inhibits reaction.	−37,330
Ca	Ca_3N_2	500°	Rapid with glowing.	−70,550
Sr	Sr_3N_2	300° to 400°	Rapid.	−76,790
Ba	Ba_3N_2	560°		−72,790
Mg	Mg_3N_2	560°	MgO is a catalyst. Reversible, $P_{N_2} = 1$ atm at 1100°.	−100,780
La	LaN	450°		−64,650
Be	Be_3N_2	900°	Reversible at 2200°.	−121,400
B	BN	> 1200°		−27,690
Al	AlN	800°		−50,050
Ti	TiN	> 800°		−74,040
Si	Si_3N_4	1300°		−154,740
Cr	CrN	580° to 800°		−22,520

[a] See Trautz and Kipphan, *Z. anal. Chem.*, **78**, 353 (1929). The reaction is autocatalytic.

[b] Kelley, "The Thermodynamic Properties of Metal Carbides and Nitrides," Bureau of Mines Bulletin 407 (1937).

Attempts to cause carbon and nitrogen to combine to form cyanogen, C_2N_2, have always met with failure. Indeed, thermodynamic studies indicate that cyanogen is not to be expected, either at high or low temperatures, to result by the direct combination of carbon and nitrogen. Thus, for $2C(s) + N_2(g) = C_2N_2(g)$, $\Delta H_{298} = 70{,}560$ cal, $\Delta S^\circ_{298} = 9.3$ cal/deg, $\Delta F^\circ_{298} = 67{,}780$ cal; and since ΔS° and ΔC_P will not suffer great changes on going to higher temperatures, one may expect ΔF°_T to be positive even at the temperatures of the electric arc.

A mixture of hydrogen, carbon, and nitrogen reacts slowly at 1900° to 2100°K to give HCN [von Wartenberg, *Z. anorg. Chem.*, **52,** 299 (1907)]; an approximate free energy equation for $C(s) + \frac{1}{2}H_2(g) + \frac{1}{2}N_2(g) = HCN(g)$ is $\Delta F^\circ_T = 31{,}000 - 10T$. The accepted value of $\Delta F^\circ_{298.1}$ is 27,730 cal [Latimer, *Oxidation Potentials,* Prentice-Hall, New York]. At 800°K the reaction $NH_3(g) + C(s) = HCN(g) + H_2(g)$ comes to a measurable equilibrium state with $K_{atm} = P_{H_2}P_{HCN}/P_{NH_3} = 5.8 \times 10^{-6}$ [Badger, *J. Am. Chem. Soc.*, **46,** 2166 (1924)]. Calcium carbide reacts with nitrogen at about 1000° to form cyanamide $CaCN_2$; calcium fluoride and chloride act as catalysts for the reaction. A mixture of sodium carbonate, carbon, and nitrogen will react at around 1000° to give sodium cyanide. (See the section on Fixation of Nitrogen, p. 70.)

The nitrides of the metals hydrolyze more or less readily to form ammonia and the metal hydroxide or oxide. Alkali and alkaline earth nitrides undergo hydrolysis on exposure to moist air or on the addition of cold or warm water, but boron nitride requires hot water or steam to bring about its hydrolysis. Silicon and titanium nitrides are very resistant to the action of water, acids, and alkalis, and treatment of them with these reagents even in a heated sealed bomb causes only a small amount of hydrolysis.

Active nitrogen

If nitrogen at moderately low pressures (about 2 mm) is subjected to the action of a silent electric discharge, a yellow glow is observed, and this glow will persist for a time after the electric current is disconnected. The time of persistence of the glow depends principally on the size of the containing vessel. Thus, in a 24-liter flask the yellow glow may be visible for as long as 110 minutes, while with small vessels this time is much shorter [see, for example, Bay and Steiner, *Z. phys. Chem.*, **9B,** 127 (1930); Kaplan, *Phys. Rev.*, **37,** 1409 (1931); E. P. Lewis, *Astrophys. J.*, **17,** 258 (1903); Rayleigh, *Proc. Roy. Soc.*, **151A,** 567 (1935); Willey, *J. Chem. Soc.*, 142 (1932); *Proc. Roy. Soc.*, **152,** 158 (1935)]. The glowing or active nitrogen is more reactive with some substances than is ordinary nitrogen. For example, active nitrogen converts white phosphorus into red phosphorus and some phosphorus nitride, combines with sodium at 150°, forms HCN with acetylene, and decomposes NO into nitrogen and oxygen. Small amounts of impurities, Hg(g) and O_2, appear to be necessary in order to obtain active nitrogen having an appreciable length of life. The activity is due to the presence of both metastable activated nitrogen molecules and atoms. The activation energy of the molecules is said to be 6.14 electron volts and that of the atoms 2.37 to 3.56 electron volts.

The Oxides of Nitrogen

Formation

The known oxides of nitrogen are presented in the following list:

Formula	Name	State at Room Temperature	Color
N_2O	Nitrous oxide	Gas	Colorless
NO	Nitric oxide	Gas	Colorless
N_2O_3	Nitrogen sesquioxide	Gas	Red-brown
NO_2	Nitrogen dioxide	Gas	Red-brown
N_2O_4	Nitrogen tetroxide	Gas-Liq.	Colorless
N_2O_5	Nitrogen pentoxide	Solid	Colorless
NO_3	Nitrogen trioxide	—	—

Nitrous oxide is a gaseous compound and is formed in small quantities in the reduction of nitrites and nitrates by a variety of reducing agents (for example, H_2S, H_2SO_3, $SnCl_2$, Na amalgam, metals). It is produced quantitatively in the slow, spontaneous decomposition of alkaline hyponitrites [Abel, Orlich, and Proisl, *Monatshefte*, **72,** 1 (1938)],

$$N_2O_2^= + 2H^+ = N_2O + H_2O$$

and results also from the decomposition of nitrogen compounds whose empirical formula is $N_2O \cdot (H_2O)_n$. Of these substances, solid ammonium nitrate is by far the most convenient and cheapest for the preparation of N_2O. The dry salt NH_4NO_3 (m.p. 169.6°) is heated to about 170–260° for a conveniently rapid decomposition; a mixture of sodium or potassium nitrate and ammonium sulfate will, when heated to 170–260°, yield N_2O, and provides a very cheap source of the gas. Attention should be called to the fact that very rapid heating of ammonium nitrate may cause it to explode, although as ordinarily carried out the decomposition of the molten salt takes place smoothly at a rate that appears to depend only on the temperature. The decomposition by heat of NH_4NO_3 yields only a small amount of nitric oxide, NO, and this may be removed by passing the raw gas through a solution of $FeSO_4$ (the complex $FeNO^{++}$ is formed). Nitrous oxide is moderately inert toward oxidizing and reducing agents; it will support combustion, but does not initiate it except at higher temperatures. It decomposes spontaneously and with a measurable rate into N_2 and O_2 when heated to 565–850°. With water at low temperatures, it forms the hydrate $N_2O \cdot 6H_2O$, from which the pure oxide may be obtained by warming. It is used as an anesthetic in dentistry and obstetrics. Because of the solubility of N_2O in ordinary cream, it has found its chief commercial use in the preparation of *whipped* cream.

Nitric oxide, NO, is a substance of paramount importance to modern civilization, since it is formed at one stage in the principal methods used for the manufacture of nitric acid, a substance which has almost endless applications. Inasmuch as NO, although relatively inert, has a strong thermodynamic tendency to decompose into its elements at room temperatures, it is necessary to bring about its formation from N_2 and O_2 at very high temperatures or by the catalytic oxidation of ammonia. The nature of the former reaction may be judged by the following free-energy equation [see, for example, Giauque and Kemp, *J. Chem. Phys.*, **6**, 40 (1938)]

$$\tfrac{1}{2}O_2 + \tfrac{1}{2}N_2 = NO \qquad \Delta F^\circ_{298} = 20{,}650 \text{ cal}$$
$$\Delta F^\circ_T = 21{,}600 - 2.50T \text{ (from equilibrium data)}$$

At equilibrium and at 2400°C, air contains only 2.23% by volume of NO, at 3200°C about 4.4%. In the process of manufacture, air is passed through an electric arc the temperature of which is estimated to be some 3500°; by rapidly cooling the heated equilibrium mixture (the rate of decomposition of NO is slow even at 1500°), a mixture of air containing 2% or 3% nitric oxide is obtained.

A large quantity of nitric oxide is now manufactured by the oxidation of ammonia on platinum gauze or other catalysts. The mixture of air (7.5 volumes) and ammonia (1 volume) is passed very rapidly through metal tubes containing fine platinum gauze; if the gas mixture is preheated to some 500°, the oxidation at the gauze proceeds automatically. The heat of reaction contributes to the maintenance of the rather high temperature of the gauze. The presence of water vapor is advantageous in the oxidation.

$$4NH_3 + 5O_2 = 4NO + 6H_2O, \qquad \Delta F^\circ_{298} = -229{,}416 \text{ cal}$$

The large negative value of ΔF°_{298} shows the great thermodynamic tendency for this reaction to take place even at 25°C. There is a still greater thermodynamic tendency for the oxidation to proceed to the formation of nitrogen instead of nitric oxide.

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O, \qquad \Delta F^\circ_{298} = -312{,}056 \text{ cal}$$

and, in the absence of the platinum gauze catalyst, nitrogen is one of the principal products of the reaction when NH_3 burns in an atmosphere of O_2. At room temperatures neither reaction takes place, in spite of the great tendency indicated by the ΔF values, that is, the reactions are very slow; but at 500° and on the platinum surface, the rate of formation of NO predominates over that to form nitrogen. We have here again a case in which the factors governing the yield of the desired product are those involving rates alone. In the arc process, the yield of NO is governed mainly by the small thermodynamic tendency for the reaction to take place.

Although large quantities of NO are formed in the arc and ammonia oxidation processes, little if any is compressed into steel cylinders and thus marketed. The main reason for this is that NO reacts, at room temperature, moderately rapidly with oxygen to form nitrogen dioxide, and it is to this form that most of the NO formed is unavoidably converted; another reason is that the demand for pure NO as such is not great. For experimental purposes, there are a number of reactions which yield NO as a purifiable product. By far the most convenient and best of these reactions, from the point of view of purity of products, is that between nitrous acid and potassium iodide. Fifty per cent sulfuric acid is added slowly to a solution that is 4 m in KNO_2 and 1 m in KI. The reaction is:

$$2HNO_2 + 2I^- + 2H^+ = 2NO + I_2 + 2H_2O$$

The evolved gas is passed successively through 90% H_2SO_4, 50% KOH, a trap cooled to $-75°$, and P_2O_5, and finally it is bubbled through liquid nitric oxide. The sulfuric acid serves to remove excess water from the gas; the KOH absorbs most of the NO_2 if any is present. Non-condensable gases are pumped off while the nitric oxide is kept frozen at liquid-air temperatures. Any N_2O is not absorbed by the alkali but dissolves in the liquid NO, in which it is very soluble. This process, if carried out carefully, yields a product containing only some 0.0008 mole per cent or less of impurities [Johnston and Giauque, *J. Am. Chem. Soc.*, **51,** 3194 (1929)]. The pure nitric oxide when liquefied has a blue color; the solid when in a clear ice-like form is also blue.

Characteristic of NO is its ability to form complexes with many metals and salts. Thus, it will replace NH_3 in $[Co(NH_3)_6]X_2$ to form $[CoNO(NH_3)_5]X_2$ if the gas is bubbled through an ammoniacal solution of the hexammine cobaltous salt; if X_2 represents halides, the product is black in color; if X_2 is sulfate, the product is red [Werner and Karrer, *Helv. Chim. Acta*, **1,** 54 (1918)]. Solutions of $FeSO_4$ absorb NO *reversibly* to form $Fe(NO)SO_4$, and the intense black or deep-red color that results serves as a basis for the detection of nitrites and nitrates. The solid red salt $FeNOSO_4$ is unstable, and, on heating its solutions, nitric oxide is evolved. The salts $FeNOSeO_4 \cdot 4H_2O$ (black) and $FeNOHPO_4$ are more stable than the sulfate [Manchot and Linckh, *Z. anorg. Chem.*, **140,** 37 (1924)]. Concentrated solutions of $CuCl_2$ or $CuBr_2$ absorb NO to give deep-blue to violet solutions of $CuNOCl_3^-$. It will be noted that usually only one and occasionally two NO are absorbed per metal atom. In H_2SO_4 solution, $Fe_2(SO_4)_3$ will form deep-red $Fe_2(NO)_4(SO_4)_3$.

The carbonyls react with nitric oxide to form nitroso compounds; thus, with $Ni(CO)_4$ blue to green and even colorless solids are formed whose compositions have not been definitely established and which decompose on heating to 90° with the emission of light [Mond and Wallis, *J. Chem. Soc.*, **121,** 32 (1922)]. With cobalt tetracarbonyl, nitric oxide forms the light yellow, volatile cobalt nitrosyl carbonyl $Co(CO)_3NO$; this compound reacts quantitatively with bromine to form $CoBr_2$, CO, and NO [Hieber and Anderson, *Z. anorg. Chem.*, **211,** 132 (1933); Coleman and Blanchard, *J. Am. Chem. Soc.*, **58,** 2160 (1936)]. When the volatile iron pentacarbonyl $Fe(CO)_5$ is heated to 45° with NO under pressure, the black, unstable tetranitrosyl compound $Fe(NO)_4$ is formed. When NO is passed through a suspension of FeS in K_2S_3 solution, the dark-colored compound $K[Fe\{FeS(NO)_2\}_3NO]$ is formed. A solution containing $FeSO_4$ and $K_2S_2O_3$ will absorb NO to form the red-brown $K[Fe(S_2O_3)(NO)_2]$. These compounds and $K_2[(NO)_2FeS_2Fe(NO)_2]$ (obtained by treating the first with alkali) are known as Roussin's salts [Hoffman and Wiede, *Z. anorg. Chem.*, **8–11** (1895–1896)]. The common, brownish-red nitroprussiate of soda, $Na_2Fe(NO)(CN)_5$, is not obtained by the direct absorption of NO but by warming $K_4Fe(CN)_6$ with dilute nitric acid and then neutralizing with Na_2CO_3 solution; with soluble sulfides the nitroprussiate reacts to form violet-colored solutions of $[Fe(CN)_5NSO]^{4+}$.

More recently the conditions under which nitric oxide can be added more readily to a metal have received further attention. When finely divided, freshly reduced cobalt is treated with a mixture of CO and NO, nitrosyl carbonyl, $Co(CO)_3NO$ (m.p. − 11°, v.p. 56 mm at 16°), is formed. The same compound is formed when an alkaline suspension of $Co(CN)_2$ is treated first with CO and then with NO. Still another reaction leads to this interesting compound; if an alkaline solution containing $CoCl_2$ and cysteine, $HSCH_2CHNH_2COOH$, is treated with carbon monoxide, the latter is absorbed and on acidification $[Co(CO)_4]_2$ rises to the surface. When nitric oxide is bubbled through this mixture, the nitrosyl carbonyl results in the form of reddish-brown vapors which may be condensed to light yellow crystals [Coleman and Blanchard, *J. Am. Chem. Soc.*, **58,** 2160 (1936); Hieber and Anderson, *Z. anorg. Chem.*, **211,** 132 (1933); see also the splendid reviews by Blanchard, *Chem. Rev.*, **21,** 3 (1937), **26,** 409 (1940)]. When NO is passed through a solution of $[Fe(CO)_4]_3$ (a solid) in $Fe(CO)_5$ (b.p. 150°) at 95°, the compound $Fe(CO)_2(NO)_2$ may be separated by distillation from the resulting mixture. It is, at room temperature, a red crystalline solid melting at 18.5°. With iodine in benzene solution, $Fe(NO)_2I_2$ is formed from the dinitrosyl iron carbonyl [Anderson, *Z. anorg. Chem.*, **208,** 238 (1932)]. The solid salts $FeCl_3$, $AlCl_3$, and $BiCl_3$ absorb nitric oxide reversibly to form $FeNOCl_3$ (red), $AlNOCl_3$, and $BiNOCl_3$ (yellow). Bivalent salts of the metals will, in general, absorb nitric oxide only when in solution (except for the ferrous phosphate and selenate mentioned above), whereas the solid trivalent salts will absorb this gas.

These addition compounds are sufficient to exhibit the ability of nitric oxide to occupy coordination positions in a manner closely similar to that shown by carbon monoxide.

Nitric oxide does not support combustion unless the temperature is rather high. This fact is sometimes adduced as evidence for believing that the NO must dissociate before the oxygen becomes active, but the argument is not convincing. If the gas is passed into an acid permanganate solution, it is oxidized to nitric acid; this reaction is the basis for a volumetric method for the determination of NO. Nitric oxide combines slowly with Br_2 and Cl_2, but not with I_2, to form the nitrosyl halides (which see), NOBr and NOCl.

Nitrogen sesquioxide, N_2O_3, is very unstable at room temperature and above; it decomposes rapidly and extensively at these temperatures and consists, in large part, of a mixture of NO and NO_2 with a small equilibrium concentration of N_2O_3. When an equimolal mixture of NO and NO_2 is condensed at −20°, a blue liquid results (b.p. 3.5°) which will solidify at −103°. N_2O_3 may be looked upon as the anhydride of nitrous acid, HNO_2. When solutions of alkali nitrites are acidified, decomposition results, gases ($NO + NO_2$) are evolved, and the solution has a definite blue color. When an equimolal mixture of NO and NO_2 is dissolved in alkaline solutions, for example KOH or NaOH, pure or almost pure nitrites result. This reaction is usually written

$$N_2O_3 + 2OH^- = 2NO_2^- + H_2O$$

although it must be understood that only a small amount of the gas mixture consists of N_2O_3. When it is dissolved in water, the reaction is not so simple as that just written; both nitrous and nitric acids are formed in the solution. With concentrated sulfuric acid the white solid nitrosyl bisulfate, $NOHSO_4$ (nitrosyl sulfonic acid), is formed, and this reaction plays an important role in the manufacture of sulfuric acid by the lead chamber process.

Nitric oxide reacts moderately rapidly with oxygen to form the brownish-red gas NO_2, nitrogen dioxide. The reaction is reversible; at room temperature the equilibrium

$$NO + \tfrac{1}{2}O_2 = NO_2$$

lies almost completely to the right; at about 750° the equilibrium constant

$$K_{\text{atm}} = \frac{P_{NO}P_{O_2}^{1/2}}{P_{NO_2}}$$

is approximately unity. The dioxide is readily and conveniently prepared for laboratory purposes by heating dry lead nitrate, $Pb(NO_3)_2$. The heating may take place in glass, but, since the lead oxide formed combines to some extent with glass, it is desirable to place the lead salt on a platinum foil in the glass flask to avoid spoiling it. Nitrogen dioxide polymerizes very rapidly and reversibly to form colorless N_2O_4.

$$2NO_2 = N_2O_4$$

Accordingly, NO_2 and N_2O_4 must be discussed together, since at ordinary temperatures both are present in the gas.

The equilibrium mixture of NO_2 and N_2O_4 can be readily condensed to a clear, faintly yellow-colored liquid which boils at 21.15° and which will freeze to a solid with a melting point of $-11.2°$.

Nitrogen dioxide ($NO_2 + N_2O_4$) is quite reactive as an oxidizing agent. Its main use in this connection is in the lead chamber process for the manufacture of sulfuric acid, where one may regard the catalytic couple as:

$$SO_2 + NO_2 = SO_3 + NO$$
$$NO + \tfrac{1}{2}O_2 = NO_2$$

although the mechanism is much more complicated than this. NO_2 does not react rapidly with CO to form CO_2 below 250°, but it does react with NH_3 to form N_2, H_2O, NO, and NH_4NO_3. It is also capable of acting as a reducing agent, being oxidized to nitric acid by $KMnO_4$ solutions, for example. The dioxide combines with liquid sulfur dioxide to form $(NO)_2S_2O_7$, which is the anhydride of nitrosyl bisulfate, $NOHSO_4$. In the lead chamber process, a mixture of NO and NO_2 dissolves in concentrated sulfuric acid to form this compound:

$$NO + NO_2 + 2H_2SO_4 = 2NOHSO_4 + H_2O$$

Nitrosyl bisulfate (also known as nitrosyl sulfate, nitrosulfuric acid, nitrosulphonic acid, and chamber crystals) is a white solid which melts with decomposition at 73° to give the anhydride $(NO_2)S_2O_7$ mentioned above. When $NOHSO_4$ is treated with water, it decomposes according to the important reversible reaction

$$2NOHSO_4 + H_2O = 2H_2SO_4 + NO + NO_2$$

Nitrogen dioxide dissolves in water to form nitric and nitrous acids according to the reversible reaction

$$2NO_2 + H_2O = H^+ + NO_3^- + HNO_2$$

In acid solution, the nitrous acid decomposes:

$$3HNO_2 = H^+ + NO_3^- + H_2O + 2NO, \qquad \Delta F^\circ_{298} = -2040 \text{ cal}$$

so that in nitric acid of moderate concentrations the principal reaction is [see Chambers and Sherwood, *J. Am. Chem. Soc.*, **59**, 316 (1937)]:

$$3NO_2(g) + H_2O = 2HNO_3(aq) + NO(g), \qquad \Delta F^\circ_{298} = -5870 \text{ cal}$$

It is clear from the small values of ΔF°_{298} that these reactions come to equilibrium at room temperature when measurable quantities of the reactants are present. It is also evident that the removal of NO favors the formation of nitric acid and the decomposition of nitrous acid; in the manufacture of nitric acid this is accomplished by having oxygen present, which reacts with the NO to form NO_2.

Nitrogen dioxide has a corrosive action on metals and is also dangerous to the health. The fumes should not be allowed to escape into rooms where people are working or where fine machinery is installed The dioxide combines with only a few substances, if any, to form addition or complex compounds.

Nitrogen pentoxide may be conveniently prepared in either one of two ways. In the first, P_2O_5 is added slowly to cooled 100% nitric acid until a paste results. The mixture is warmed to 35–40° and the N_2O_5 distilled off and condensed at −75° (solid CO_2); the product will contain some NO_2. A further distillation at room temperature in a stream of ozonized air and drying with P_2O_5 result in a pure product; the ozone oxidizes the NO_2 to N_2O_5. In the second method pure NO_2 is treated directly with ozonized oxygen. The reaction

$$2NO_2 + O_3 = N_2O_5 + O_2$$

is rapid and complete.

Nitrogen pentoxide is a white solid whose vapor pressure is 76 cm at 32.4°. It decomposes slowly at room temperature and more rapidly at higher temperatures. The study of the decomposition rate of the gas has played an important role in the theories of homogeneous gas reactions. The decomposition takes place irreversibly according to the equation

$$N_2O_5(g) = 2NO_2(g) + \tfrac{1}{2}O_2$$

and the reaction turns out to be of the first order.

Nitrogen pentoxide dissolves readily in water with the evolution of heat to form nitric acid; accordingly, N_2O_5 is the anhydride of HNO_3. With reducing agents such as metals and organic substances, N_2O_5 reacts readily and sometimes violently to form oxides, or oxides and nitrates

Nitrogen trioxide, NO_3, is said to form in a glow discharge through mixtures of NO_2 and O_2. The gases must be passed directly from the discharge tube into a strongly cooled (−185°) trap, since the NO_3 is not stable. At low temperatures it is a white solid which begins to decompose at −142°. In a 2 n HNO_3 solution it appears to be more stable; the solutions react slowly with I^- to form iodine [Schwarz and Achenbach, *Ber.*, **68B,** 343 (1935); doubts regarding the formation of NO_3 in a discharge tube have been expressed by Klemenc and Neumann, *Z. anorg. Chem.*, **232,** 216 (1937); its existence as an intermediate in gas reactions involving nitrogen oxides is frequently postulated, Crist and Wertz, *J. Chem. Phys.*, **7,** 719 (1939)].

Physical properties of the oxides of nitrogen

Owing to their great importance and interesting properties, the physical constants of the oxides of nitrogen have been studied with considerable care by several investigators. The results considered most accurate are presented in Table 5 [see Blue and Giauque, *J. Am. Chem. Soc.*, **57,** 991 (1935); Johnston and Giauque, *J. Am. Chem. Soc.*, **51,** 3194 (1929); Giauque and Kemp, *J. Chem. Phys.*, **6,** 40 (1938)].

TABLE 5
THE PHYSICAL PROPERTIES OF THE OXIDES OF NITROGEN
(0°C = 273.1°K)

	Melting Point (°K)	Heat of Fusion, ΔH (cal)	Boiling Point (°K)	Heat of Vaporization, ΔH (cal)	Heat of Formation, ΔH^0_{298} (cal)	Free Energy of Formation, ΔF^0_{298} (cal)	Standard Entropy, S^0_{298}, of Gas (cal/deg)
N_2O .	182.26	1563	184.59	3958	19,650	24,930	52.58
NO .	109.49	549.5	121.36	3292.6	21,500	20,650	50.35
NO_2 .	261.90	3502	(294.25)	9110 ($NO_2 + N_2O_4$)	7,964	12,275	57.47
N_2O_4.	261.90	3502	294.25	9110	2,239	23,440	72.73
N_2O_5.	—	—	305.5 (subl. point)	13,800	700(g) −13,100(s)	—	—
NO_3 .	—	—	—	—	13,000(?)	—	—

The heat, energy, and entropy values are for one mole of the compound in question.

N_2O

The infrared absorption spectrum of nitrous oxide can be interpreted satisfactorily only on the assumption that the molecule is linear with the two nitrogen atoms adjacent to each other, NNO [Plyler and Barker, *Phys. Rev.*, **41,** 369 (1932)]. The N–N and N–O distances are not accurately known, but the moment of inertia of the molecule as obtained from the rotational lines of its spectrum has been established as $I = 66.0 \times 10^{-40}$ g cm². The vibrational energy states of N_2O are given by the experimentally established formula

$$\epsilon_{vib.}/hc = 1288.7v_1 + 588.3v_2 + 2237.9v_3 - 3.3v_1^2 - 2.2v_2^2 - 13.8v_3^2 - 10v_1v_2 - 26v_1v_3 - 13.5v_2v_3 + 3.0l^2$$

where v_1, v_2, and v_3 are the ordinary vibrational quantum numbers and l must assume only even integral values less than or equal to v_2. The four quantum numbers v_1, v_2, v_3, and l are required because the molecule is linear. For a nonlinear triatomic molecule like NO_2 or SO_2, there are only three fundamental frequencies of vibration; but for a linear triatomic molecule there are four, two of which have the same frequency (degenerate).

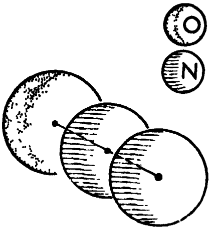


Fig. 2. The Molecular Structure of N_2O. N—N ≅ 1.12Å; N—O ≅ 1.19A. [Schomaker and Spurr, *J. Am. Chem. Soc.*, **64**, 1184 (1942).]

The vapor pressures of the solid and liquid are given by the semiempirical equations

Solid:

$$\log_{10} p_{cm} = -\frac{1286}{T} + 9.13061 - 0.0014038T$$

Liquid:

$$\log_{10} p_{cm} = -\frac{893.56}{T} + 6.72158 \qquad (182.26 - 185.85°K)$$

Heat Capacities (Molal) (cal/deg.)

T(°K)	20	50	100	150	180	185
C_P	1.51	6.52	9.90	12.19	13.98	18.57 (liq.)

The entropy of $N_2O(g)$ can be calculated from spectroscopic data and has also been carefully determined from heat-capacity measurements [Badger and Woo, *J. Am. Chem. Soc.*, **54**, 3523 (1932); Blue and Giauque, *J. Am. Chem. Soc.*, **57**, 991 (1935)]. The results are, in cal/deg mole:

	Spectroscopic Data	Heat-Capacity Measurements	Diff.
S°_{298}	52.581	51.44	1.14

The difference is explained in terms of the randomness of orientation of the N_2O molecule in the crystal at low temperatures. If this randomness were such that the molecules did not differentiate between the orientation NNO and ONN, then the experimentally found value of S°_{298} would be too small by the amount $R \log_e 2 = 1.38$ cal/deg. This is not much larger than the 1.14 cal/deg shown above. It is presumed that some randomness of orientations exists but that it is not complete.

No equilibrium measurements involving the formation of nitrous oxide have been made. All known reactions in which it enters are either irreversible or hopelessly complicated. By using the observed ΔH° and the ΔS° obtained by application of the third law of thermodynamics, it is possible to calculate an accurate value of ΔF°_{298} of formation, namely, the value 24,930 cal, shown in Table 5.

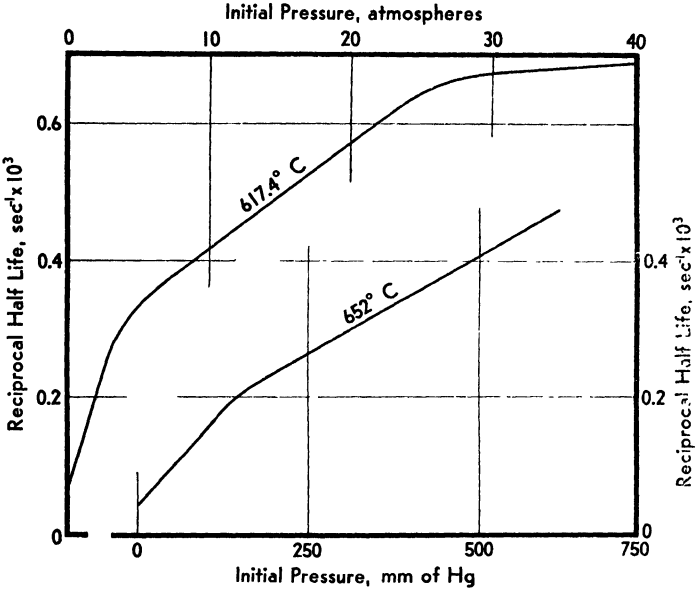


Fig. 3. The Effect of Pressure on the Thermal Decomposition of Nitrous Oxide.

In recent years added interest has been shown in the imperfections of gases both for the purposes of applied thermodynamics and for their theoretical interest. The values of the second virial coefficient B (in $PV = RT + BP$) for N_2O have been carefully determined [Johnston and Weimer, *J. Am. Chem. Soc.*, **56**, 625 (1934)] and, expressed empirically, are, in cm³/mole,

$$B = 32 - \frac{5611.5}{T} + 3.9424 \times \frac{10^6}{T^2} - 3.9145 \times \frac{10^{11}}{T^4} + 3.0747 \times \frac{10^{16}}{T^6}$$

The rate of thermal decomposition of N_2O into N_2 and O_2 has been studied in the temperature range 565° to 850°C and over a large range of pressures. The results of several investigators are shown in Fig. 3 [Hinshelwood and Burk, *Proc. Roy. Soc.*, **106,** 284 (1924); Hunter, *ibid.*, **144,** 386 (1934)]. The form of the curve is rather complex and it is improbable that the whole pressure range can be represented by any expression with a single set of constants (see Hinshelwood, *The Kinetics of Chemical Change*, p. 131, Oxford University Press, 1940).

NO

Nitric oxide gas is paramagnetic, the molal susceptibility in cgs units and gauss being 1.46×10^{-3} at 20°C [Bauer and Picard, *J. de Phys.*, **1,** 97 (1920); Sone, *Sci. Rep. Tohoku Univ.*, **11,** (3), 139 (1922); see also Van Vleck, *Phys. Rev.*, **31,** 587 (1928)]. In terms of $\mu = (3\chi_m RT/(N_0)^2)^{1/2}$, where χ_m is the molal susceptibility, N_0 is Avogadro's number, and μ is the magnetic moment in Bohr magnetons, the following values for NO have been obtained experimentally. The μ (calc.) values were obtained by use of the theory to be discussed below.

T(°K)	μ (obs.)	μ (calc.)	T(°K)	μ (obs.)	μ (calc.)
112.8	1.535	1.546	216.0	1.768	1.771
157.2	1.679	1.678	250.6	1.807	1.807
178.0	1.713	1.718	296.0	1.837	1.837

[See Bitter, *Proc. Nat. Acad.*, **15,** 638 (1929); Aharoni and Sherrer, *Z. Physik,* **58,** 749 (1929); Wiersma, deHaas, and Capel, *Comm. Leiden,* 212b.] The observed values of μ are not constant, as they would be if the electronic state of the molecule did not vary with the temperature. The results of both the magnetic measurements and the absorption spectrum of NO [Jenkins, Barton, and Mulliken, *Phys. Rev.*, **30,** 150 (1927); Gillette and Eyster, *Phys. Rev.*, **56,** 1113 (1939)] are explained as follows:

The lowest or ground state of the nitric oxide molecule has a resultant *angular momentum* due to the combined spin and orbital momenta of the odd valence electron ($5 + 6 = 11$). In this ground state, the electron spin momentum of $\frac{1}{2}$ opposes the orbital momentum of 1, so that the resultant is $1 - \frac{1}{2} = \frac{1}{2}$. Such a state is given the designation $^2\Pi_{1/2}$. It is comparatively easy to excite the molecule to another higher electronic state in which the spin and orbital momenta add to give a resultant of $1 + \frac{1}{2} = \frac{3}{2}$. This state is designated by $^2\Pi_{3/2}$; the energy difference $\Delta\epsilon$ between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states is 124.2 cm^{-1} or about 352 cal/mole. At very low temperatures all of the molecules are in the $^2\Pi_{1/2}$

state; at 121.36°K, 82.3% and at 298°K, 34.5% of the molecules are in this lower $^2\Pi_{1/2}$ state.

The resultant *magnetic moment* of the molecule in the $^2\Pi_{1/2}$ state is zero while that in the $^2\Pi_{3/2}$ state corresponds to two Bohr magnetons. Consequently, at very low temperatures $\mu = 0$ and at very high temperatures $\mu = 2$. At intermediate temperatures the values of μ will lie between these two extremes, and the table shows this to be the case experimentally. It is evident that to calculate the susceptibility χ_m or the magnetic moment μ one must make use of the distribution law, and this has been done by Van Vleck [*Electric and Magnetic Susceptibilities*, Oxford University Press, 1932, p. 269], who finds that

$$\mu = 2\left\{\frac{1 - e^{-x} + xe^{-x}}{x + xe^{-x}}\right\}^{1/2}$$

$$x = \frac{\Delta\epsilon}{kT}.$$

The calculated values of μ are shown in the table under μ(calc.); the agreement with experiment is excellent.

There is another interesting property of the NO molecules. The resultant (spin + orbital) electronic angular momentum vector $\mathbf{\Omega}$ of the odd electron may be directed in one of two directions parallel to the line joining the nuclei. Whether $\mathbf{\Omega}$ is directed toward the nitrogen atom or toward the oxygen atom might appear, at first sight, to make no difference in energy between the two states, but application of the quantum theory shows that the energies will be different. As a matter of fact, the energy difference is very small for nitric oxide, but it is nevertheless observable, some absorption bands exhibiting a doubling (λ-type doubling).

There are, then, two types of doubling in the nitric oxide molecule, namely, that corresponding to the two electronic states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, and that known as λ-type doubling. The effect of the λ doubling is, for all ordinary chemical purposes, to introduce an additional weight of 2 in the Boltzman factors, and in entropy calculations this results in an additive term $R \log_e 2$ [Johnston and Chapman, *J. Am. Chem. Soc.*, **55**, 153 (1933)].

We may next enquire about the rotation states of the molecule as a whole. If $\mathbf{N}$ is the vector corresponding to the angular momentum of the rotating nuclei, N—O, then the resultant angular momentum will be the quantum theoretical vector sum, $\mathbf{J}$, of $\mathbf{N}$ and $\mathbf{\Omega}$. If $\mathbf{J} = \mathbf{\Omega} + \mathbf{N}$, then $J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \cdots$ for the $^2\Pi_{1/2}$ state and $J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2} \cdots$ for the $^2\Pi_{3/2}$ state. It is only $\mathbf{J}$ that is quantized, not $\mathbf{N}$. $\mathbf{\Omega}$ is directed along the figure axis of the molecule when $\mathbf{N}$ is not large, but for large $\mathbf{N}$ the electron spin aligns itself with the vector sum of the electronic orbital momentum

L and **N**; this fact may be looked upon as the result of the magnetic field produced by the rotating nuclei and their electrons, which produce for large **N** a greater interaction with the electron spin vector **S** than the field due to the electrons. The least value of J is $\frac{1}{2}$ ($^2\Pi_{1/2}$ state) or $\frac{3}{2}$ ($^2\Pi_{3/2}$ state), and the weight factors are $2J + 1$.

The vibrational and rotational energy levels of nitric oxide are given by the following formulas which express the results of experiment [Gillette and Eyster, *Phys. Rev.*, **56,** 1113 (1939)].

$$\epsilon_i(J, v) = \epsilon_e + G_i(v) + B_v \left\{ (J + \tfrac{1}{2})^2 - 1 + (-1)^i \left[(J + \tfrac{1}{2})^2 - \frac{A}{B_v} + \frac{A^2}{4B_v} \right]^{1/2} \right\} + D_v J^2 (J + 1)^2$$

$$G_i(v) = \omega_{ei}(v + \tfrac{1}{2}) - \omega_e x_e (v + \tfrac{1}{2})^2 + \omega_e y_e (v + \tfrac{1}{2})^3$$

$$B_v = B_e - \alpha(v + \tfrac{1}{2})$$

$i = 1$ for $^2\Pi_{1/2}$ state; $i = 2$ for $^2\Pi_{3/2}$ state

$\omega_{e1} = 1904.03\ \text{cm}^{-1}$ $B_e = 1.7046\ \text{cm}^{-1}$

$\omega_{e2} = 1903.68\ \text{cm}^{-1}$ $\alpha = 0.0178\ \text{cm}^{-1}$

$\omega_e x_e = 13.97\ \text{cm}^{-1}$ $I_e = 16.423 \times 10^{-40}\ \text{g cm}^2$

$\omega_e y_e = -0.00120\ \text{cm}^{-1}$ $r_e = 1.1508\ \text{Å}$

$A = 124.2\ \text{cm}^{-1}$ $D_0 = -5 \times 10^{-6}\ \text{cm}^{-1}$

A is the separation of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states.

The molecular constants and energy states of NO as derived from spectroscopic measurements have been employed in the calculation of entropies and free energies. A summary of the results of the calculations and experiments are shown in Table 6 [see Johnston and Giauque, *J. Am. Chem. Soc.*, **51,** 3194 (1929); Nernst, *Z. anorg. Chem.*, **49,** 213 (1906)].

It will be noted that the experimental and calculated values of $S°$ differ by 0.75 cal/deg. This is, within the experimental error, equal to $\frac{1}{2}R \log_e 2$, namely, 0.69. The difference is explained by assuming that in the solid form nitric oxide is present as double molecules N_2O_2, and further that there is a limited randomness in orientation of these molecules in the crystals. If the randomness is of only a twofold nature—that is, if the N_2O_2 molecules fail to differentiate only between the N_2O_2 and O_2N_2 orientations—then, since one mole of NO corresponds to $\frac{1}{2}$ mole of N_2O_2, the experimental $S°$ (NO) will be too small by

$$\tfrac{1}{2}R \log_e 2 = 0.69$$

This compares well with the 0.75 cal/deg found. Further evidence for the dimeric form of solid nitric oxide is provided by the fact that the solid is diamagnetic.

The second virial coefficient, B (in $PV = RT + BP$), for NO has been accurately determined by Johnston and Weimer [*J. Am. Chem. Soc.*, **56,**

TABLE 6
THE PHYSICAL AND MOLAL THERMODYNAMIC PROPERTIES OF NO
(0°C = 273.1°K)

Vapor Pressure

Solid, $\log_{10} p_{cm} = -867/T + 0.00076T + 9.05125$
Liquid, $\log_{10} p_{cm} = -776/T - 0.002364T + 8.562128$
Melting point, 109.49°K Boiling point, 121.36°K
$\Delta H_{109.49}$ (fusion) = 549.5 cal $\Delta H_{121.36}$ (vaporization) = 3292.6 cal

Heat Capacities, Solid and Liquid

Solid		Liquid	
T(°K)	C_P (cal/deg)	T(°K)	C_P (cal/deg)
19.51	1.590	112.81	16.067
39.20	4.060	115.79	16.915
62.32	6.016	120.56	18.667
88.96	7.795		
102.55	8.713		

Entropy of Gas at 1 atm (calc.)

T(°K)	$S°$ (cal/deg)	T(°K)	$S°$ (cal/deg)
1	10.62	500	54.06
10	25.48	1000	59.39
50	36.90	2000	65.28
298.1	50.35	5000	73.53

T(°K)	$S°$ (calc.)	$S°$ (obs.)
121.36	43.75	43.0
298.1	50.35	49.60

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) = NO(g)$; $\Delta H^\circ_{298} = 21{,}500$ cal; $\Delta F^\circ_{298} = 20{,}650$ cal;
$K = P_{NO}/P^{1/2}_{N_2}P^{1/2}_{O_2}$

T(°K)	K (calc.)	K (obs.)	T(°K)	K (calc.)	K (obs.)
298.1	7.26×10^{-16}	—	2675	7.98×10^{-2}	5.8×10^{-2}
1000	8.86×10^{-5}	—	3000	1.24×10^{-1}	—
1500	3.30×10^{-3}	—	3500	2.09×10^{-1}	—
1811	1.14×10^{-2}	0.93×10^{-2}	4000	3.07×10^{-1}	—
2033	2.21×10^{-2}	1.6×10^{-2}	5000	5.26×10^{-1}	—

625 (1934)] and is given in cm^3/mole, as a function of the temperature, by

$$B = 20 + \frac{5881.5}{T} - 5.7639 \times \frac{10^6}{T^2} + 8.4301 \times \frac{10^{10}}{T^4} - 9.2783 \times \frac{10^{14}}{T^6}$$

Nitric oxide reacts with hydrogen at a measurable rate in the temperature range 900–1100°K. The reaction is homogeneous in quartz vessels and at pressures above 400 mm, and it is of the third order [Hinshelwood and Green, *J. Chem. Soc.*, **129**, 730 (1926)].

$$2NO + 2H_2 = N_2 + 2H_2O$$

$$-\frac{d(NO)}{dt} = k(NO)^2(H_2)$$

The rate constants are shown plotted in Fig. 4, and are given in cc^2 mole^{-2} sec^{-1} by the empirical equation

$$\log_{10} k = -\frac{38689.5}{T} - 66.37 \log T + 245.410$$

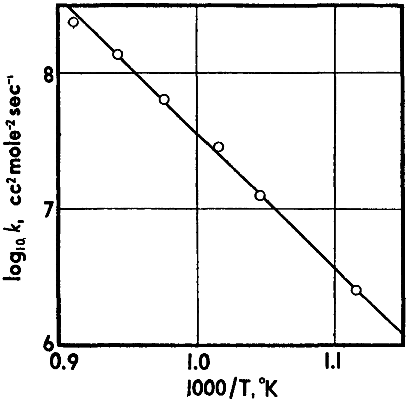


Fig. 4. The Thermal Rate of Reaction Between Nitric Oxide and Hydrogen. $-d(NO)/dt = 2k(NO)^2(H_2)$.

N_2O_3

The instability of N_2O_3 has made it not feasible to investigate its properties as thoroughly as those of other oxides of nitrogen. The equilibrium $N_2O_3(g) = NO_2(g) + NO(g)$ has been studied by Verhoek and Daniels [*J. Am. Chem. Soc.*, **53**, 1250 (1931)] with the following results. Corrections for the N_2O_4 present were, of course, necessary.

$$K = \frac{P_{NO_2}P_{NO}}{P_{N_2O_3}}$$

$$25° \; K_{P\,atm} = 2.105 - 45.63C^{\circ}_{N_2O_3} \qquad \Delta F^{\circ}_{298} = -441 \text{ cal}$$
$$35° \; K_{P\,atm} = 3.673 - 78.11C^{\circ}_{N_2O_3} \qquad \Delta F^{\circ}_{308} = -796 \text{ cal}$$
$$45° \; K_{P\,atm} = 6.880 - 196.4C^{\circ}_{N_2O_3} \qquad \Delta F^{\circ}_{318} = -1218 \text{ cal}$$
$$\Delta H^{\circ} = 10{,}300 \text{ cal}$$
$$N_2 + \tfrac{3}{2}O_2 = N_2O_3 \quad \Delta F^{\circ}_{298} = 33{,}805 \text{ cal}$$

$C^{\circ}_{N_2O_3}$ = Concentration in mole/liter of N_2O_3 if none had decomposed.

(Boiling point N_2O_3(l), 3.5°; melting point, −103°.)

That the values of K_P show a dependence on the pressure through the factor $C^{\circ}_{N_2O_3}$ arises from the fact that the gases in equilibrium are not perfect. The boiling and melting points given for the blue liquid and solid are very approximate; the liquid doubtless contains dissolved NO and NO_2.

NO_2

Nitrogen dioxide gas is paramagnetic, and the measured susceptibility corresponds to one (the odd) electron spin; that is to say, only an electron spin moment contributes to the magnetic moment of the molecule. The ground state of the molecule is accordingly designated by $^2\Sigma$. There is no effect due to a resultant orbital moment, since this, unlike that in NO, has been somehow destroyed by the additional oxygen atom. This is expressed by saying $S = J = \frac{1}{2}$, $L = 0$. Accordingly, the g-factor,

$$g = 1 + \frac{S(S + 1) + J(J + 1) - L(L + 1)}{2J(J + 1)}$$

is equal to 2 and

$$\chi_m = \frac{(N\mu_0)^2 S(S + 1)4}{3RT} + N\alpha$$

where $N\alpha$ is a small, negative correction term that accounts for the diamagnetism. Since oxygen is also paramagnetic ($S = 2 \times \frac{1}{2} = 1 = J$), it is found convenient to use it as a standard in measurements on gases. It is found experimentally [Havens, *Phys. Rev.*, **41,** 337 (1932)] that

$$\frac{\chi_m(NO_2)}{\chi_m(O_2)} = 0.390, \qquad \chi_m(O_2) = \frac{1.0}{T}$$

Theory gives a ratio of 0.375. The agreement is quite satisfactory and justifies the assumption that for NO_2, $S = J = \frac{1}{2}$. In the lowest rotational, vibrational, and electronic state of the NO_2 molecule, there still remains the spin momentum $S = \frac{1}{2}$, and the weight of this state will be $2S + 1 = 2$. At the lowest temperatures at which heat capacities are ordinarily measured, namely 13°K, the degeneracy of the $^2\Sigma$ state will not be removed, and to the measured entropy the amount $R \log_e 2$ will have to be added to bring accord with the value calculated from molecular data.

The fundamental vibrational frequencies of NO_2 are $\omega_1 = 641$, $\omega_2 = 1373$, and $\omega_3 = 1615$ cm^{-1}, and none of these is degenerate. The molecule is triangular in shape, but the exact determination of its structure has been a difficult problem. By combining the results of thermal and equilibrium measurements with spectroscopic data, the product of the moments of inertia has been evaluated, $I_1I_2I_3 = 1.44 \times 10^{-116}$ g^3 cm^6 [Giauque and Kemp, *J. Chem. Phys.*, **6,** 40 (1938)]. The most probable structure is N—O distance 1.21 Å, and angle O—N—O 141° [recalculation by R. A. Spurr, using the radial distribution method, from electron-diffraction data of Maxwell and Mosley, *J. Chem. Phys.*, **8,** 738 (1940)].

As noted above, nitrogen dioxide at ordinary temperatures always contains some N_2O_4 in equilibrium with the NO_2. This fact renders the treatment of thermodynamic data more complicated than is the case with the other substances discussed so far. The following data for the solid, liquid, and vapor refer to the mixture.

TABLE 7

THE PHYSICAL AND MOLAL THERMODYNAMIC PROPERTIES OF NITROGEN DIOXIDE

(0°C = 273.1°K)

Vapor Pressure

Solid, $\log_{10} p_{cm} = -2460.000/T + 9.58149 + 7.61700 \times 10^{-3}T - 1.51335 \times 10^{-5}T^2$

Liquid, $\log_{10} p_{cm} = -1753.000/T + 9.00436 - 11.8078 \times 10^{-4}T + 2.0954 \times 10^{-6}T^2$

Melting point = 261.90°K Boiling point = 294.25°K

Heat Capacities

Solid				Liquid	
T(°K)	C_P (cal/deg)	T(°K)	C_P (cal/deg)	T(°K)	C_P (cal/deg)
20	2.03	150	18.36	270	32.93
50	8.70	200	21.92	280	33.28
100	14.51	250	25.63	290	33.71

ΔH (fusion) = 3502 cal ΔH (evaporation) = 9110 cal at b.p.

$S^\circ_{298.1}$ (equil. mixture at 1 atm pressure) = 80.62 cal/deg

$S^\circ_{298.1}$ (NO_2 gas) = 57.47 cal/deg S°_{298} (N_2O_4(g)) = 72.73 cal/deg

The equilibrium constants of the reaction $N_2O_4 = 2NO_2$ have been measured by several experimenters. The results of Verhoek and Daniels [*J. Am. Chem. Soc.*, **53**, 1250 (1931)] appear to be the most accurate.

$$K_{atm} = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

$$25^\circ \quad K_{atm} = 0.1426 - 0.7588C^\circ_{N_2O_4}$$

$$35^\circ \quad K_{atm} = 0.3183 - 1.591C^\circ_{N_2O_4}$$

$$45^\circ \quad K_{atm} = 0.6706 - 3.382C^\circ_{N_2O_4}$$

$$\Delta H^\circ = 14{,}600 \text{ cal} \qquad \Delta F^\circ_{298} = 1154 \text{ cal}$$

where $C^\circ_{N_2O_4}$ is the concentration of N_2O_4 in moles per liter that would be present if all NO_2 were in that form. The additive term $C^\circ_{N_2O_4}$ arises from the fact that the gases NO_2 and N_2O_4 are not perfect. When the results of several investigators are taken together, $\Delta H^\circ_{298} = 13{,}693$ cal and $\Delta F^\circ_{298} = 1{,}110$ cal, for the reaction written $N_2O_4(g) = 2NO_2(g)$, with all energy quantities corrected to those for the hypothetical perfect gas state.

There remains to be discussed the moderately slow, reversible reaction

$$NO_2 = NO + \tfrac{1}{2}O_2$$

taking place in the gas phase. The results of Bodenstein and Linder

[*Z. phys. Chem.* **100,** 82 (1922)], as recalculated by Giauque and Kemp, are as follows:

TABLE 8
EXPERIMENTAL EQUILIBRIUM CONSTANTS FOR THE REACTION
$NO_2(g) = NO(g) + \frac{1}{2}O_2(g)$

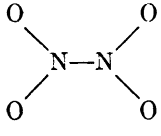
$T(°K)$	$K_{atm} = \frac{P_{NO}P_{O_2}^{1/2}}{P_{NO_2}}$	
298.1	$7\ 229 \times 10^{-7}$	Extrapolated Values
400	$2\ 534 \times 10^{-4}$	
450	1.384×10^{-3}	
500	$8\ 006 \times 10^{-3}$	Range of Measurements
600	$8\ 082 \times 10^{-2}$	
700	$4\ 220 \times 10^{-1}$	
800	1.469	
900	3.870	

It is evident from these equilibrium constants that NO_2 is extensively decomposed, at ordinary pressures, at 900°K; at room temperature the decomposition is slight.

The vibrational levels of N_2O_4 have been studied by Sutherland [*Proc. Roy. Soc.*, **141A,** 342 (1933)] and have the following fundamental frequencies:

$$\omega_1 = 1265 \quad \omega_2 = 1360 \quad \omega_3 = 752 \quad \omega_4 = 813 \quad \omega_5 = 1744$$
$$\omega_6 = 1744 \quad \omega_7 \text{ (torsional)} = ? \quad \omega_8 = 283 \quad \omega_9 = 380$$
$$\omega_{10} = 500 \quad \omega_{11} = (380) \quad \omega_{12} = (500) \text{ cm}^{-1}$$

When all of the thermodynamic and spectroscopic data are combined, the entropies of NO_2 and N_2O_4, as well as the products of the moments of inertia of these molecules, are calculable. The results indicate, but do not prove, that the N_2O_4 molecule has a symmetrical planar structure



The rate of combination of NO and O_2 is measurable, and the reaction proves to be one of the third order. Investigations of the reverse reaction show it to be of the second order.

$$2NO + O_2 = 2NO_2$$

$$\frac{d(NO_2)}{dt} = k_f(NO)^2(O_2) \qquad \text{(formation)}$$

$$-\frac{d(NO_2)}{dt} = k_d(NO_2)^2 \qquad \text{(decomposition)}$$

The values of k_t and k_d are shown in the following table [Bodenstein, *Z. phys. Chem.*, **100,** 68 (1922); Breiner, Pfeiffer, and Malet, *J. chim. phys.*, **21,** 25 (1924)].

T(°K)	$k_t \times 10^{-9}$ cm^6 mole^{-2} sec^{-1}	T(°K)	k_d cm^3 mole^{-1} sec^{-1}
273.1	7.88	592	498
333.2	5.58	603.5	775
470.0	3.34	627	1810
563.6	2.82	651.5	4110
661.9	2.54	656	4740

Aside from being one of the few known third-order gas reactions, it is also one whose rate decreases with increase in temperature. In Fig. 5 is shown a function of the rate constants k plotted against $1000/T$.

The rapidity and reversibility of the reaction

$$2NO_2(g) = N_2O_4(g)$$

have been noted above. The equilibrium states can be determined without great difficulty, but the rate of the reaction is so rapid that accurate measurements have not been possible. Historically, the importance of this reaction depended on the possibility that its rate might be greater than the rate of activation of the N_2O_4 molecules by any known mechanism. There are reactions which are doubtless as rapid as this one but which do not appear to be so convenient to study experimentally. Two methods have been used in the measurements; in one of these, the velocity of sound as a function of the frequency is measured and the theory of the effect as given by Einstein is applied to the results [Einstein, *Sitzb. Berl. Acad.*, 380 (1920)]. According to this theory, the velocity of sound should increase when the frequency of the compressional sound waves reaches or exceeds such a magnitude that equilibrium is not attained during a quarter-cycle. It turns out, however, that a variety of factors prevent the theory from being reliably applicable to experimental results, not the least being the failure of some of the internal energy states of the molecules to adjust themselves to the temperature changes occurring during the very rapid adiabatic compressions and expansions arising when sound traverses a gas [see Kistiakowsky and Richards, *J. Am. Chem. Soc.*, **52,** 4661 (1930); Richards and Reid, *J. Chem. Phys.*, **1,** 737 (1933)]. The results of experiment show that there is no change in the velocity of sound through NO_2—N_2O_4 mixtures at frequencies ranging as high as 80,000 cycles/sec. In the second method the gas is expanded through small holes in a platinum diaphragm into a long tube and allowed finally to condense in a liquid air trap. Small thermocouples placed at intervals along the long tube serve to determine the temperature of the gas; the temperature decreases until the dissociation of the N_2O_4 is complete. Since the heat of the reaction $N_2O_4 = 2NO_2$ is appreciable, 14,000 cal, the temperature drop is much greater than that corresponding to the Joule-Thomson effect. The results, while subject to some uncertainty, doubtless give the order of magnitude of the rate of decomposition of N_2O_4 [Brass and Tolman, *J. Am. Chem. Soc.*, **54**, 1003 (1932)].

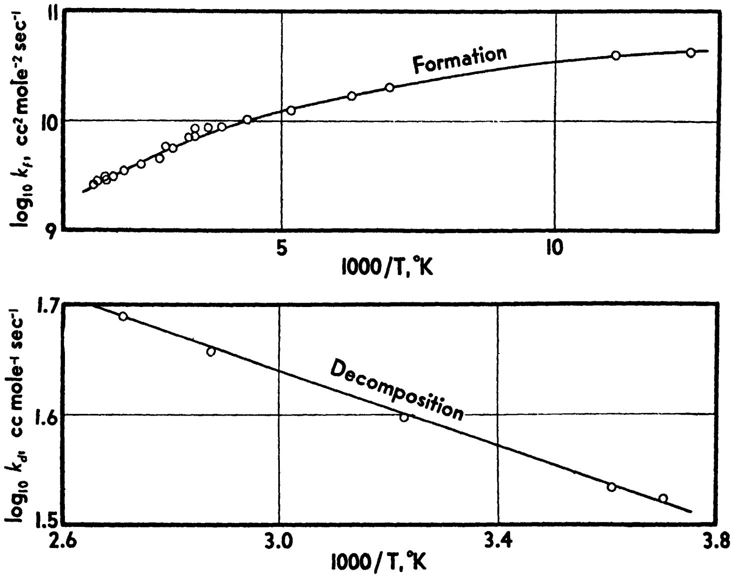


Fig. 5. The Thermal Decomposition and Formation of Gaseous Nitrogen Dioxide. $-d(O_2)/dt = k_f(O_2)(NO)^2$; $-d(NO_2)/dt = k_d(NO_2)^2$.

$$-\frac{d(N_2O_4)}{dt} = k(N_2O_4)$$

$$k = 15\ \text{sec}^{-1}\ \text{at} \approx -15°;$$

$$k \approx 6 \times 10^4\ \text{sec}^{-1}\ \text{(calc.) at}\ 25°.$$

This rate is appreciably less than the rates of activation by collision as calculated from the accepted theories. Nitrogen tetroxide is not, therefore, a substance whose rate of decomposition cannot be adequately explained by molecular collision theories.

N_2O_5

Nitrogen pentoxide is a white, volatile, crystalline solid at room temperatures. The following table of vapor pressures shows that even at room temperatures the substance is near the sublimation point [Daniels and Bright, *J. Am. Chem. Soc.*, **42,** 1131 (1920)].

Table 9
THE VAPOR PRESSURES OF NITROGEN PENTOXIDE
[$N_2O_5(s) = N_2O_5(g)$]

T(°K)	p_{mm}	T(°K)	p_{mm}	T(°K)	p_{mm}
243.0	3	273.0	51	293.0	279
263.0	21	283 0	118	305.5	760

$$\log_{10} p_{mm} = \frac{1244}{T} + 34.1 \log_{10} T - 85.929$$

$$\Delta H^\circ = 13{,}800 \text{ cal} \qquad \Delta F^\circ_{298} = 32 \text{ cal} \qquad \Delta F^\circ_T = 13{,}800 - 45.22T$$

Nitrogen pentoxide is an unstable substance, and even at room temperature the gas decomposes slowly into NO_2 and O_2.

$$N_2O_5(g) = 2NO_2 + \tfrac{1}{2}O_2$$

In spite of the fact that two molecules Nof $_2O_5$ are required to yield one of O_2, the decomposition rate is first-order.

$$-\frac{d(N_2O_5)}{dt} = k(N_2O_5)$$

The vapor pressures given in the table have been corrected for the decomposition taking place during the measurements. The rate of decomposition has been studied repeatedly and it has played an important role in the theories of reaction rates. The reason for this is that the reaction is a homogeneous one, and the rate constants are independent of the pressure even when this is as low as 0.01 mm. At still lower pressures, the constants show a decrease. In Fig. 6 are shown $\log_{10} k$ plotted against $1000/T$ for measurements made at low-to-moderate pressures, 0.01 mm to 760 mm, by a number of investigators [see, for example, Hodges and Linhorst, *Proc. Natl. Acad. Sci.*, **17,** 28 (1931); Schumacher and Sprenger, *ibid.*, **16,** 129 (1930); Ramsperger and Tolman, *ibid.*, **16,** 6 (1930); Daniels, Wulf and Karrer, *J. Am. Chem. Soc.*, **44,** 2402 (1922)]. It does not seem possible that the slow step in the

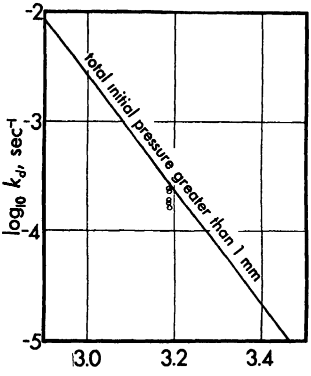


Fig. 6. The Thermal Decomposition of Nitrogen Pentoxide at Normal and Very Low Pressures. $-d(N_2O_5)/dt = k_d (N_2O_5)$. The total initial pressures at the points designated by the small circles are, in descending order: 0.0470, .0142, .0056, .0085, .0073 mm.

reaction is $N_2O_5 = 2NO_2 + O - 61{,}000$ cal, since this would require the absorption of much more energy than is available. A more reasonable mechanism and the one ordinarily proposed is

$$\begin{aligned} N_2O_5 &= N_2O_3 + O_2 && \text{(slow)} \\ N_2O_3 &= NO + NO_2 && \text{(rapid)} \\ N_2O_5 + NO &= 3NO_2 && \text{(rapid)} \end{aligned}$$

It has been shown by Busse and Daniels that the rate of oxidation of NO by N_2O_5 is very rapid [*J. Am. Chem. Soc.*, **49**, 1257 (1927)].

We have already remarked that ozone oxidizes NO_2 to N_2O_5 rapidly and completely. It would appear at first sight that in a mixture of N_2O_5 and O_3 at room temperatures, the ozone would disappear at a rate dependent only on the pressure of N_2O_5, since ozone itself decomposes only very slowly at room temperatures. It is found, however, that the ozone is catalytically decomposed by the lower oxides of nitrogen, and consequently the rate of oxygen formation is more rapid than that found for the decomposition of N_2O_5 alone. The values of k are shown in the accompanying tabulation; the rate equation is

t(°C)	k in $(\text{cm}^3\ \text{mole}^{-1})^{1/3}\ \text{sec}^{-1}$
20	0.0245
25	.0420
35	.135
36	.145

$$-\frac{d(O_3)}{dt} = 2k(N_2O_5)^{2/3}(O_3)^{2/3}$$

The mechanism suggested for the reaction is

$$\begin{aligned} N_2O_5 &= N_2O_3 + O_2 = NO + NO_2 + O_2 && \text{(slow)} \\ N_2O_3 + N_2O_5 &= 4NO_2 && \text{(rapid)} \\ N_2O_3 + O_3 &= 2NO_2 + O_2 && \text{(rapid)} \\ NO_2 + O_3 &= NO_3 + O_2 && \text{(rapid)} \\ NO_3 + NO_3 &= 2NO_2 + O_2 && \text{(rapid)} \\ NO_3 + NO_2 &= N_2O_5 && \text{(rapid)} \end{aligned}$$

although it is not free from criticism. It postulates the existence of the compound NO_3, to which reference has already been made [White and Tolman, *J. Am. Chem. Soc.*, **47**, 1240 (1925); Schumacher and Sprenger, *Z. phys. Chem.*, **2B**, 267 (1929); Nordberg, *Science*, **70**, 580 (1929)].

The Sulfides of Nitrogen

There are two or possibly three well-defined sulfides of nitrogen:

NS_2 (Red liquid. Nitrogen disulfide.)
N_4S_4 (Yellow or orange-yellow solid. Nitrogen tetrasulfide.)
N_2S_5 (Red liquid, steel-gray solid below 10°, the m.p. Nitrogen pentasulfide.)

The first of these has been prepared only in small amounts and has not been extensively investigated [Usher, *J. Chem. Soc.*, **127**, 730 (1925)].

N_4S_4

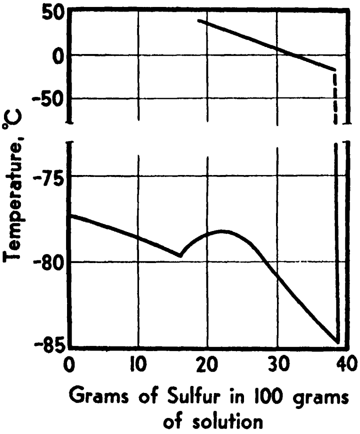


Fig. 7. The Sulfur-liquid Ammonia System. The lower curve shows the temperature at which crystallization begins; the solubility of sulfur in liquid ammonia is shown by the upper curve. The maximum in the freezing-point curve corresponds to $S(NH_3)_6$; the nearly constant solubility of sulfur with temperature indicates the existence of a compound $S(NH_3)_3$ [Ruff and Hecht].

The most important of this group of compounds is nitrogen tetrasulfide. It may be prepared in several ways, of which the two following give the best yields. (1) Dry ammonia diluted with air is passed through an ice-cold mixture of SCl_2 (250 g) and benzene (2 liters). The mixture becomes completely black in the course of about five minutes, and the fumes formed are first white, then violet, then brown, and finally yellow in color. The treatment with NH_3 is continued at room temperature for 4 to 5 hours, when the mixture becomes chocolate-brown to orange-red in color. The precipitate of NH_4Cl, N_4S_4, and S which forms is filtered or pressed free from the solvent and is then extracted with successive portions of benzene or, better, with benzene in a Soxlet apparatus. Another method of treating the precipitate consists in mixing with distilled water to dissolve and remove the NH_4Cl and then dissolving the residue in CS_2. Crystallization from benzene or CS_2 yields golden-yellow to orange-red crystals. The solvent separated from the original precipitate also contains an appreciable amount of recoverable N_4S_4 [Ruff and Geisel, *Ber.*, **37,** 1573 (1904); **38,** 2659 (1905); Schenk, *Ann.*, **290,** 171 (1896); Francis and Davis, *J. Chem. Soc.*, **85,** 259 (1904)]. Purification of N_4S_4 is effected by recrystallization from carbon disulfide solution; to remove free sulfur, the carbon disulfide solutions may be shaken with mercury. To obtain the purest product, the solid N_4S_4 is sublimed at 100° over silver gauze in an evacuated container. It has been found by Van Valkenburgh and Bailar [*J. Am. Chem. Soc.*, **47,** 2134 (1925)] that better yields (65%) are obtained by treating a mixture of S_2Cl_2 (5 cc) and ether (150 cc) with ammonia gas. The reactions of formation are, essentially,

$$5SCl_2 + 16NH_3 = N_4S_4 + 12NH_4Cl + S$$
$$6S_2Cl_2 + 16NH_3 = N_4S_4 + 12NH_4Cl + 8S$$

(2) Sulfur dissolves slowly in liquid ammonia at −11.5° or higher to form electrically conducting solutions of N_4S_4, $(NH_4)_2S$, and $(NH_4)_2S_x$,

according to the reversible reactions

$$10S + 16NH_3(l) = N_4S_4 + 6(NH_4)_2S \text{ [in } NH_3(l)]$$
$$(NH_4)_2S \text{ [in } NH_3(l)] + XS = (NH_4)_2S_{X+1} \text{ [in } NH_3(l)]$$

Equilibrium appears to be attained slowly between the dissolved substances, and the concentration of N_4S_4 at equilibrium appears to be much less than that of the dissolved sulfur. The solution of the sulfur is accompanied by changes in color: at 15° the first more dilute solutions are dirty green to green in color; and as the concentration of S increases, the color becomes first blue and finally red. The amount of sulfur that dissolves in $NH_3(l)$ depends on the temperature: at 70° the saturated solution contains about 4% of sulfur; at 20°, it contains about 36%, and the solubility then varies but little with temperature, even down to −85°. At −84.6° the compound $S(NH_3)_3$ is present in the saturated solution; at −78.3° the freezing point of the solutions goes through a maximum when the ratio of S to NH_3 corresponds to $S(NH_3)_6$. The blue color of the dilute solutions mentioned above is ascribed to these addition compounds by some investigators [Ruff and Hecht, *Z. anorg. Chem.*, **70,** 49 (1911)]. In order to obtain the N_4S_4 formed in the above reversible reactions, it is necessary to remove the $S^=$ or $S_x^=$, and this is accomplished by adding AgI, which is very soluble in liquid ammonia, to the sulfur-ammonia solutions. After filtering, the filtrate is evaporated to obtain the N_4S_4 [Ruff and Geisel, *Ber.*, **38,** 2659 (1905); Bergstrom, *J. Am. Chem. Soc.*, **48,** 2319 (1926)].

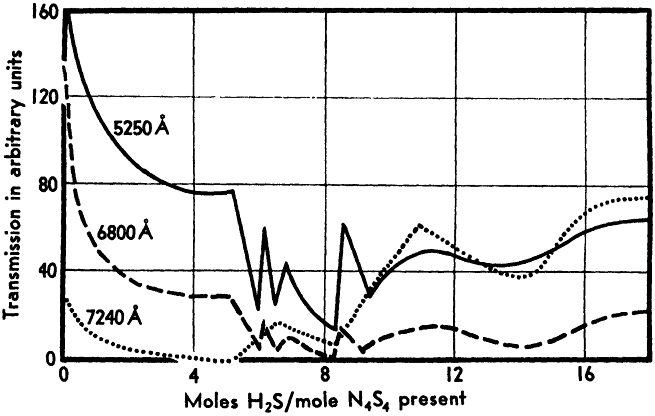


Fig. 8. The Light Transmission of Solutions Containing Both H_2S and N_4S_4 in Liquid Ammonia. The various maxima and minima may indicate the existence of a number of sulfur nitrogen compounds. The diagram also shows the colors of the solutions [Ruff and Hecht].

It has been stated above that the reaction between S and NH_3(l) is reversible. This is confirmed by three facts, namely: on evaporating the solutions to dryness, practically pure sulfur is obtained as a residue; on treatment of the solutions with silver iodide and filtering off the Ag_2S, a yellow solution of N_4S_4 results; and if a liquid ammonia solution of N_4S_4 is treated with H_2S, solutions identical with those obtained on mixing S and NH_3(l) are obtained [Ruff and Hecht, *loc. cit.*]. The studies made by Ruff and Geisel on the S-NH_3 solutions were mainly physical-chemical in nature. Bergstrom attacked the problem from a purely chemical point of view and found, for example, that while solutions of N_4S_4 alone in NH_3(l) do not react with alkali cyanides to give thiocyanates, the solutions of S or S + $(NH_4)_2S$ in NH_3(l) do yield KCNS when treated with KCN. These facts furnish added evidence for the existence of the reversible reactions written above.

Nitrogen tetrasulfide forms golden-yellow or orange-red monoclinic crystals which melt with some decomposition at about 179° and appear to boil at about the same temperature. The crystals may be sublimed in vacuum without difficulty; the sublimate has a specific gravity of 2.24 at 18° and an index of refraction of 2.046 to 1.908 for visible light. When struck, N_4S_4 will explode; it is because of this property that it is said to be dangerous to keep the solid in glass-stoppered bottles, since when the bottle is opened or closed the contents may explode. However, it is also reported that the pure solid is nonexplosive except when heated to 195° [Arnold, Hugill, and Hutson, *J. Chem. Soc.*, 1645 (1936)]. The formula N_4S_4 has been established by determinations of the freezing-point lowering of its solutions in naphthalene and in benzene [Van Valkenburgh and Bailar, *loc. cit.*] and the boiling-point elevation of solutions in CS_2, C_6H_6, and $CHCl_3$. The tetrasulfide is not wetted by water and consequently reacts only slowly with this solvent. The products of the slow hydrolytic reaction with water alone are $SO_3^=$, $S_5O_6^=$, NH_4^+, and S, and the resulting solutions are neutral to methyl-red and methyl-orange. Constant shaking is necessary in order to effect appreciable reaction. About 23% of the sulfur from the N_4S_4 appears in the form of pentathionate ion, $S_5O_6^=$. The rate of hydrolysis of N_4S_4 is more rapid in alkaline solutions, the products being $SO_3^=$, $S_2O_3^=$, and small amounts of $S^=$ and possibly $S_2O_6^=$.

Nitrogen tetrasulfide dissolves in a number of organic solvents. The table on page 37 presents the solubilities in grams of N_4S_4 per liter of solution for three common solvents [Vosnessensky, *J. Russ. Phys. Chem. Soc.*, **59**, 221 (1927)].

In liquid ammonia at 100°, N_4S_4 forms, instead of the normal yellow or orange-red, bluish violet solutions; but on evaporation the residue is N_4S_4 and not some new compound. At ordinary or moderately low temperatures, 15° to −40°, the yellow to red liquid ammonia solutions of N_4S_4 are converted, by gradual addition of H_2S, to solutions whose color varies from the original orange-red to green, then blue, and finally orange-red again. The blue color is most intense when the molal ratio of H_2S to N_4S_4 is about 6:1, and such a mixture corresponds in color and composition to that resulting from the solution of S alone in $NH_3(l)$. The addition of H_2S to the N_4S_4 solutions reverses the reaction attending solution of sulfur.

Temp. (°C)	CS_2	C_6H_6	C_2H_5OH
0	3.705	2 266	0.645
10	6 845	4 260	.830
20	9.391	6.301	1.050
30	13.188	8 692	1.271
40	16 887	11.107	1.478
50	—	13.721	1.640
60	—	17.100	—

With dry $NH_3(g)$, N_4S_4 forms the addition compound $N_4S_4{\cdot}2NH_3$; the vapor pressure of ammonia above this compound is appreciable and indicates that the absorption of ammonia takes place reversibly. Liquid ammonia solutions of N_4S_4 react with PbI_2 and other metallic salts to yield compounds such as $PbN_2S_2{\cdot}NH_3$; when this compound is warmed, the NH_3 is driven off, and the resulting PbN_2S_2 formed explodes [Ruff and Geisel, *Ber.*, **37**, 1579 (1904)].

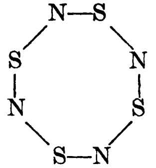
A suspension of N_4S_4 in CS_2 reacts with chlorine, the color of the mixture changing from orange-red to olive-green and finally to brownish red. On cooling the resulting solution, pale-yellow crystals of $N_4S_4Cl_4$ separate. The compounds $N_4S_4Br_6$ and $N_4S_5Br_2$ have also been reported.

When N_4S_4 is refluxed with four parts of acetyl chloride, CH_3COCl, the yellow compound N_3S_4Cl, thiotrithiazyl chloride, results. A solution of N_3S_4Cl in ice water yields a precipitate of N_3S_4I when treated with an ice-cold solution of potassium iodide. A solution of S_2Br_2 in CS_2 reacts with N_4S_4 to form the yellow N_3S_4Br. The nitrate, $N_3S_4NO_3$, bisulfate, $N_3S_4HSO_4$, and thiocyanate are also known. These compounds are almost salt-like in character; because of their interesting nature and properties, they deserve further study.

When N_4S_4 is treated with cold S_2Cl_2, a black, crystalline compound with a green luster is formed whose formula is $N_4S_6Cl_2$. Still another derivative of N_4S_4, namely, $N_4S_4H_4$, is formed when N_4S_4 is reduced in a benzene-alcohol mixture with $SnCl_2$. The $N_4S_4H_4$ decomposes, on heating to 100–145°, into S, N_4S_4, and NH_3; it is evidently the analogue of $N_4S_4Cl_4$ [see Meusen, *Ber.*, **62,** 1959 (1929)].

As remarked above, nitrogen tetrasulfide sublimes readily. If the vapors pass through quartz wool heated to 300° and are then allowed to condense, N_4S_4 condenses first, and in the still cooler portions of the apparatus a compound is observed which is blue by transmitted light but bronze-colored by reflected light. This blue compound was shown by Burt [*J. Chem. Soc.*, **97**, 1171 (1910)] to have the empirical formula $(NS)_x$, and he believed it to be an isomer of N_4S_4. Vosnessensky [*J. Russ. Phys. Chem. Soc.*, **61**, 1317 (1929)] is said to have proved that the blue or bronze-colored compound is not an isomer of N_4S_4, but possibly a form of elementary sulfur. It is not so readily soluble in organic solvents as is the ordinary N_4S_4.

The structure of N_4S_4 has recently been established by the electron diffraction method to be an eight-membered, cradle-shaped ring with N – S = 1.62Å, S – S = 2.69Å, S – N – S = 112°, and N – S – N = 106.° This structure is consistent with the volatility of the substance and its ability to form addition compounds of the type $N_4S_4Cl_4$. [Lu and Donohue, *J. Am. Chem. Soc.*, **66**, 818(1944).]



The fact that KCN does not react with liquid ammonia solutions of N_4S_4 indicates that the sulfur atoms are not bonded to each other. The further fact that the compounds $N_4S_4Cl_4$ and $N_4S_4H_4$ are readily formed, with the Cl or H probably bonded to S atoms, provides some evidence for believing that four of the 44-valence electrons in N_4S_4 are more readily available for bond formation than the remaining 40. The ring structure proposed is in accord with the moderate volatility of the compound. Through resonance among several structures the four extra electrons could make for a structure which, on the average, would be symmetrical.

Nitrogen tetrasulfide is the analogue of NO; this compound in the solid state is diamagnetic and exists as N_2O_2, but there is no evidence for the existence of N_4O_4.

N_2S_5

This compound is obtained as a deep-red oil (specific gravity, 1.901 at 18°) when N_4S_4 (30 g) is heated for two hours at 100° with very pure CS_2 (500 cc). After cooling and filtering, the solvent is distilled off and the residue is digested with dry ether (500 cc) in which N_2S_5 is soluble. Any dissolved sulfur present in the ether is precipitated out by cooling to –25° and shaking for an hour. The sulfur is filtered off and the filtrate is allowed to evaporate in a moisture-free atmosphere. The dark-red oil that remains will solidify to a crystalline mass on cooling to −15°. The crystals are steel-gray in color and resemble iodine in appearance; they melt at 10–11° to give the dark-red oil, and both the solid and liquid forms have a very strong and disagreeable odor [Murthmann and Clever, *Z. anorg. Chem.*, **13**, 200 (1897); *Ber.*, **29**, 340 (1896)]. On heating, the liquid slowly decomposes into nitrogen and sulfur. The compound is not soluble in water but decomposes in contact with it to ammonia and sulfur; in this respect it does not resemble its analogue N_2O_5, which dissolves in water to give nitric acid. Nitrogen pentasulfide is soluble to the extent of from 8 to 12% in CS_2 and from 2 to 3% in ether, but is difficultly soluble in benzene and alcohol. The solutions are stable in the dark but are decomposed by light [see also Van Valkenburgh and Bailar, *J. Am. Chem. Soc.*, **47**, 2134 (1925)]. It has been suggested by Usher that the red oil known as N_2S_5 may be a solution of sulfur in one of the lower sulfides.

When N_4S_4 in carbon disulfide solution is treated with NO_2, the white, solid oxysulfide, $(NSO_4)_x$, results. $N_5S_6O_4$ (yellow) and $N_4S_8O_6$ (yellow) are also known [Murthmann and Clever, *loc. cit.*].

NS_2

If a mixture of N_4S_4 and sulfur is vaporized at 125°, a small amount of red liquid resembling liquid bromine in its intensity and shade of color collects on the cold walls of the distilling apparatus [Usher, *J. Chem. Soc.* **127**, 730 (1925)]. The red liquid is moderately volatile and has a composition corresponding to NS_2. It is readily soluble in benzene, chloroform, carbon disulfide, and ether, and at room temperatures it slowly decomposes into a mixture which has the appearance of solid N_4S_4 and sulfur. That the correct molecular formula is NS_2 seems doubtful; even NO_2 shows a marked tendency to polymerize, and in analogy with N_4S_4 one would expect NS_2 to have the formula N_2S_4 at the very least.

Another compound of nitrogen and sulfur having a composition corresponding to NS_2 has been described by Moldenhauer and Zimmerman [*Ber.*, **62**, 2390 (1929)] as resulting from the action of active nitrogen on sulfur. A silent electric discharge between aluminum electrodes is passed through nitrogen at pressures under 12 mm; the active nitrogen thus formed is allowed to react with the sulfur present in the discharge tube. For reaction the temperature of the sulfur is held at 80–90°. A black or blue-black substance having the odor of iodine collects on the walls of the reaction vessel. The solid is extracted with CS_2 to remove elementary sulfur. Further purification of the residue leads to a black solid having the composition NS_2. On heating in a dry, evacuated container it undergoes a change, without the formation of free nitrogen, to deep-brown fumes which condense to a red oil. The black or blue-black solid may be a polymerized form of the red NS_2 found by Usher.

Still another nitrogen sulfide is formed when N_4S_4 is passed over silver gauze at 125°. In the cooler parts of the vessel, a ruby-red liquid collects which, when warmed to 50° or kept for from one-half hour to two days at room temperature, becomes blue in color; this blue substance resembles that resulting from the vaporization of N_4S_4 through quartz wool heated to 300° [Usher, *loc. cit.*].

N_4Se_4

Nitrogen tetraselenide is formed when Se_2Cl_2 in CS_2 is treated with ammonia. In glacial acetic acid the molecular weight determined from freezing-point depressions is 341 to 357; the formula weight of N_4Se_4, namely 373, is in accord with that found experimentally. Qualitatively the properties of N_4Se_4 recall those of N_4S_4 [see Van Valkenburgh and Bailar, *loc. cit.*].

CHAPTER 2

Nitrogen Oxyhalides and Oxyacids. The Fixation of Nitrogen

The Nitrogen Oxyhalides

Nitrosyl halides

Although nitrosyl fluoride, NOF, can be prepared by the direct combination of NO and F_2, nitrosyl chloride is the usual starting point in its preparation. The NOCl vapor is passed over dry AgF; the reaction is

$$NOCl(g) + AgF(s) = NOF(g) + AgCl(s)$$

Silver fluoride is frequently employed to replace combined chlorine or bromine by fluorine. Another convenient method for the preparation of NOF is by the decomposition of $NOBF_4$ with NaF [Baly and Mailander, *Z. anorg. Chem.*, **217**, 161 (1934)]. The nitrosylfluoborate can be prepared by saturating concentrated HBF_4 with N_2O_3.

$$2HBF_4 + N_2O_3 = 2NOBF_4 + H_2O$$

The $NOBF_4$, which precipitates out as a white, hydroscopic solid, can be dried and further purified by sublimation. When it is heated to 300°C with NaF, the following reaction takes place:

$$NOBF_4 + NaF = NaBF_4 + NOF$$

A copper or platinum vessel should be used for the decomposition, since NOF readily attacks glass at high temperatures.

Nitrosyl fluoride is a colorless gas melting at $-132.5°$ and boiling at $-59.9°$. At room temperature the dry gas attacks glass only slowly. Reaction with water or moist air is rapid, and nitric, nitrous, and hydrofluoric acids and nitric oxide are formed. The reactions are,

$$NOF + H_2O = HNO_2 + HF \text{ primarily}$$
$$3\ HNO_2 = H^+ + NO_3^- + 2NO + H_2O \text{ when } (H^+) \text{ is large}$$

Nitrosyl chloride is an orange-yellow gas at room temperature and a deep-red liquid when condensed (b.p. $-6.4°$). It may be prepared in several ways, the purity of the product being dependent on the method used. Thus, when *aqua regia,* a mixture of strong nitric and hydrochloric acid, is heated, nitrosyl chloride is one of the products, the others being NO_2, Cl_2, and H_2O. It is believed that the action of *aqua regia* on the noble metals, Au and Pt, is due to nitrosyl chloride. A very simple method for the preparation of nitrosyl chloride takes advantage of the remarkable reaction

$$2NO_2(g) + KCl(s) = KNO_3(s) + NOCl(g)$$

which takes place at room temperature [Whittaker, Lundstrom, and Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931)]. The potassium chloride must contain a small amount of moisture (2.4%), the role of which is not clear. In practice the moistened KCl crystals are placed in long glass tubes, through which NO_2 is allowed to stream. If the product still contains some NO_2, it may be recirculated through the column of KCl.

Another and common method for preparing nitrosyl chloride consists in the direct combination of NO and Cl_2. This reaction takes place at a measurable rate at room temperature and more rapidly at higher temperatures. Owing to the fact that the reaction is reversible,

$$2NO + Cl_2 = 2NOCl$$

it is not possible to prepare absolutely pure NOCl; at room temperature, NOCl decomposes to the extent of about 0.5%. The extent of the decomposition increases with temperature and is easily measurable above 125°.

Nitrosyl chloride reacts rapidly with water to form nitric, nitrous, and hydrochloric acid together with nitric oxide, and it is corrosive in its action on many metals. In the vapor phase it reacts rapidly and reversibly with iodine to form iodine monochloride.

$$2NOCl(g) + I_2(g) = 2NO(g) + 2ICl(g)$$

The rate of the reaction is much greater than the rate of decomposition of NOCl alone; accordingly, the iodine must react directly with nitrosyl chloride and not simply with the chlorine resulting from its decomposition.

Nitrosyl bromide, NOBr, is not obtainable in the pure state, since it decomposes reversibly to some extent (about 7% at 1 atm pressure of NOBr) even at room temperature. The decomposition is less at 0°C and becomes quite extensive at 200°. The vapor is red in color and condenses to a dark-red liquid (b.p. $\approx$ 0°). Nitrosyl bromide is best prepared by allowing nitric oxide and bromine to come together. The rate of the third-order reaction is slow enough to be measured at room temperature. (See Fig. 9.)

$$2NO(g) + Br_2 = 2NOBr$$

The compound is also formed when nitric oxide is bubbled through liquid bromine, although the resulting vapors contain considerable nitric oxide and bromine in addition to nitrosyl bromide.

Nitrosyl bromide, like the chloride, reacts readily with water to form nitric, nitrous, and hydrobromic acid along with nitric oxide. When gaseous NOBr and chlorine are brought together, a rapid reversible reaction takes place with the formation of NOCl, Br_2, NO, and BrCl, these substances in addition to NOBr and Cl_2 being present in equilibrium with each other. It is to be noted that whereas the gas phase reactions $2NO + Cl_2 = 2NOCl$, $2NO + Br_2 = 2NOBr$, and $Br_2 + Cl_2 = 2BrCl$ are slow at room temperature, a mixture of NO, Cl_2, and Br_2 reacts very rapidly to form the equilibrium mixture; this suggests that one or more of the following reactions is very rapid: $NOCl + \frac{1}{2}Br_2 = NOBr + \frac{1}{2}Cl_2$, $NOBr + \frac{1}{2}Cl_2 = NOCl + \frac{1}{2}Br_2$, and NOCl or $NOBr + BrCl = NOCl + Br_2$.

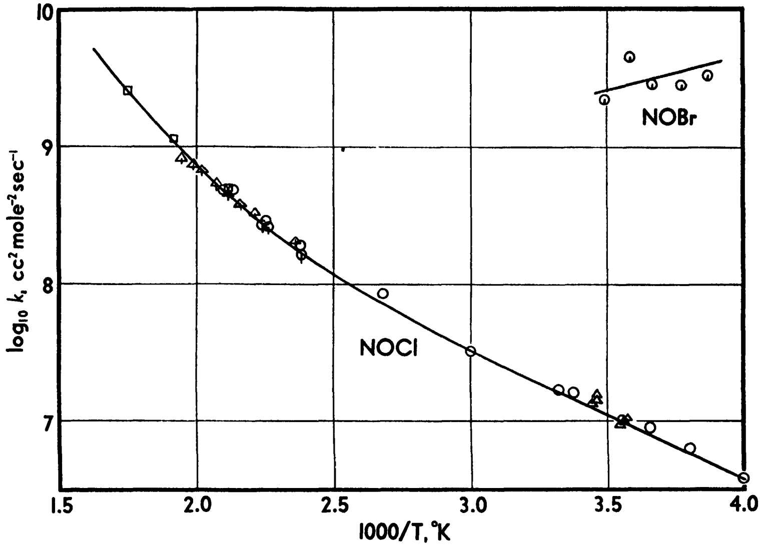


Fig. 9. The Rate of Formation and Decomposition of NOCl **and** NOBr. $d(NOX)/dt = k(NO)_2(X_2)$, X = Cl or Br. NOBr, ⊙ Trautz and Dalal [*Z. anorg. Chem.*, **102,** 149 (1918)]. NOCl, ○ Welinsky and Taylor, formation; □ Welinsky and Taylor, decomposition [*J. Chem. Phys.*, **6,** 466 (1938)]; ⍋ Waddington and Tolman, decomposition [*J. Am. Chem. Soc.*, **57,** 689 (1935)]; △ Trautz and Heglein [*Z. anorg. Chem*, **110,** 233 (1920)]; ♀ Trautz (*Z. anorg. Chem.*, **86,** 254 (1914)] recalculated by Welinsky.

The rates of combination of NO and Cl_2 and Br_2 have been measured by several investigators. The rate of decomposition of NOCl has also been studied. Representative results are as follows [NOCl, Welinsky and Taylor, *J. Chem. Phys.*, **6,** 466 (1938); NOBr, Trautz and Dalal, *Z. anorg. Chem.*, **102,** 149 (1918)]:

$$\frac{d(NOCl)}{dt} = k_1(NO)^2(Cl_2) \qquad \text{(formation)}$$

$$-\frac{d(NOCl)}{dt} = k_2(NOCl)^2 \qquad \text{(decomposition)}$$

Temp. (°C)	$k_1 \times 10^{-7}$ cm^6 mole^{-2} sec^{-1}	Temp. (°C)	k_2 cm^3 mole^{-1} sec^{-1}
−25	0.404	200	76
0.0	.897	250	1,100
22.0	1.60	300	10,100
60.0	3.55		
100.0	8.35		

$$\frac{d(\mathrm{NOBr})}{dt} = k(\mathrm{NO})^2(\mathrm{Br_2}) \qquad \text{(formation)}$$

$$k = 3.0 \times 10^{10} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1} \text{ at } 0^\circ$$

It must be noted that these rate expressions do not hold when equilibrium is being approached; the more exact equation would be

$$\frac{d(\mathrm{NOCl})}{dt} = k_1(\mathrm{NO})^2(\mathrm{Cl_2}) - k_2(\mathrm{NOCl})^2$$

where $d(\mathrm{NOCl})/dt$ now means the net change in (NOCl) with time both near and far from equilibrium. At equilibrium $d(\mathrm{NOCl})/dt = 0$ and $(\mathrm{NO})^2(\mathrm{Cl_2})/(\mathrm{NOCl})^2 = k_2/k_1 = K$, the equilibrium constant. Evidently, if K and either k_1 or k_2 are known, then the other rate constant may be calculated. These reactions are two of the small number of third-order homogeneous gas reactions. In Fig. 9 are shown plots of $\log_{10} k$ against $1000/T$ for the nitrosyl halide reactions.

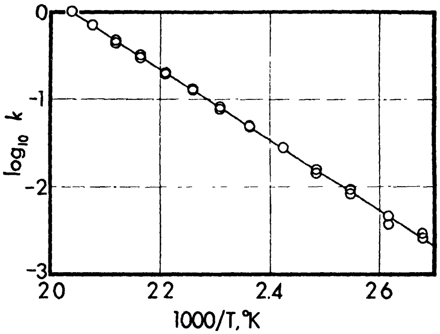


Fig. 10. Dissociation of Nitrosyl Chloride. $K_{cm} = (\mathrm{NO})^2(\mathrm{Cl_2})/(\mathrm{NOCl})^2$.

The equilibrium states in the nitrosyl halide reactions have been studied with considerable care, especially so in the case of $2\mathrm{NO} + \mathrm{Cl_2} = 2\mathrm{NOCl}$. The results are shown in Fig. 10 and expressed by the following free-energy equations [Beeson and Yost, *J. Chem. Phys.*, 7, 44 (1939); Blair, Brass, and Yost, *J. Am. Chem. Soc.*, **56,** 1916 (1934)]:

$$2\mathrm{NOCl(g)} = 2\mathrm{NO(g)} + \mathrm{Cl_2(g)}$$

$$\Delta F^\circ_T = 16429 - 18.967T \log_{10} T + 21.452T + 0.010708T^2 - 2.4208 \times 10^{-6}T^3 \pm 40 \text{ cal}$$

$$\Delta S^\circ_T = -13.215 + 18.967 \log_{10} T - 0.021416T + 7.2625 \times 10^{-6}T^2 \pm 0.3 \text{ cal/deg}$$

$$2\mathrm{NOBr(g)} = 2\mathrm{NO(g)} + \mathrm{Br_2(g)}$$

$$\Delta F^\circ_T = 8780 - 30.88T \log_{10} T + 51.26T + 0.0186T^2 - 5.8 \times 10^{-6}T^3 \text{ cal}$$

The thermodynamic constants of NOCl as determined from equilibrium measurements are not in agreement with those calculated from spectroscopic data. The discrepancy seems to be due to the incorrect interpretation of the infrared absorption spectrum rather than to any uncertainty in principle or in the nature of the NOCl molecule (NOCl(g) is diamagnetic).

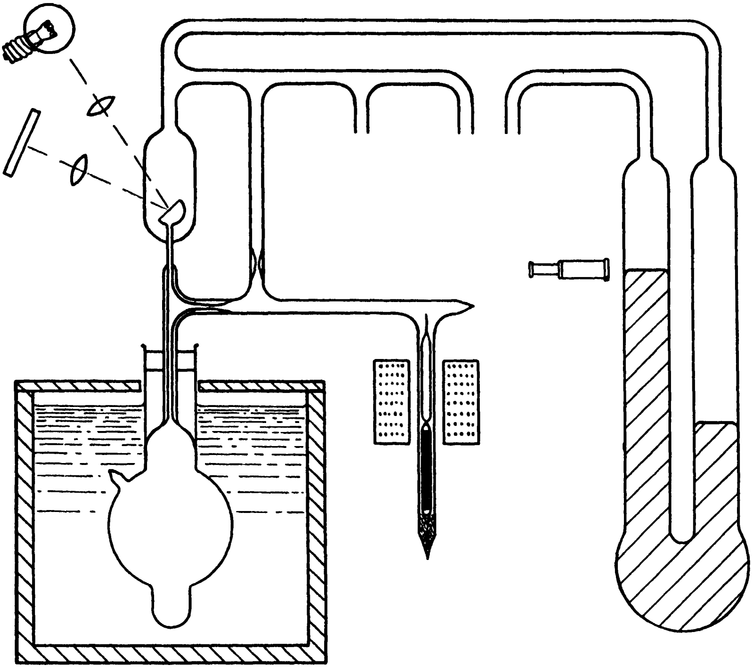


Fig. 11. A Typical Apparatus for the Measurement of Equilibria Involving Corrosive Gases. The pressures are measured by means of an all-glass click gauge which may be silvered on its outer surface; the changes of pattern with pressure are observed on a screen.

In order to correct the observed pressures of the equilibrium mixtures for gas imperfections, the virial coefficients B in $PV = RT + BP$ were determined for NOCl over a moderate range of temperatures.

t(°C)	0	25	50	75	100
$-B$, cm^3 mole^{-1}	389	307	253	218	196

Both NOCl and NOBr are nonlinear molecules; accordingly, they are examples of molecules having no rotational symmetry. The internuclear distances and bond angles are shown in Fig. 12 [Ketelaar and Palmer, *J. Am. Chem. Soc.*, **59,** 2629 (1937)].

TABLE 10
THE THERMODYNAMIC CONSTANTS OF NOCl AND NOBr

	ΔF°_{298} Formation (cal)	ΔH° Formation (cal)	S°_{298} (cal/deg)	Melting Point (°C)	Boiling Point (°C)
NOCl(g)	15,790	12,496	63.0	−64.5	−6.4
NOBr(g)	19,255	15,810	65.2	−55.5	≈ 0°

Fundamental frequencies NOCl: 1832, 633, and 290(?) cm^{-1}

Nitryl halides

Of these compounds only two are known, namely, NO_2F and NO_2Cl. NO_2F is a colorless, rather reactive gas (m.p. −166°, b.p. −72.4°) which results, among other substances, when NO and F_2 are brought together. It reacts with heated glass and it hydrolyzes rapidly when passed into water, the products of hydrolysis being nitric and hydrofluoric acids [Ruff, Menzel, and Neumann, *Z. anorg. Chem.*, **208,** 293 (1932)].

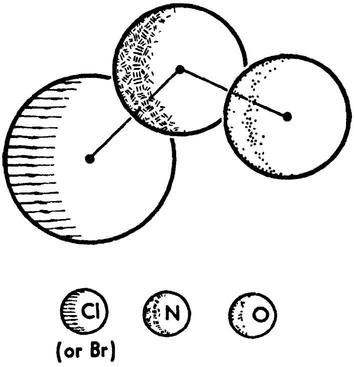


Fig. 12. The Molecular Structure of NOCl and NOBr.

	N—X	N—O	∠X—N—O
NOCl...	1.95Å	1.14Å	116°
NOBr...	2.14	1.15	117

Nitryl chloride, NO_2Cl, cannot be prepared by the direct reaction between NO_2 and Cl_2, although many efforts have been made to bring about the combination. A successful method was found in the oxidation of NOCl by ozone [Shumacher and Sprenger, *Z. anorg. Chem.*, **182,** 139 (1929)].

$$NOCl(g) + O_3(g) = NO_2Cl(g) + O_2(g)$$

The reaction is rapid and complete. NO_2Cl is a colorless gas at ordinary temperatures which condenses to a colorless liquid or a white crystalline solid at lower temperatures (m.p. −145°, b.p. −15.9°). Representative values of the vapor pressure of the liquid NO_2Cl are as follows:

T(°K)...	193.6	207.2	218.5	228.3	237.0	253.6
p_{mm}...............	16.1	51.4	115.7	209.0	319.8	648.7

and the uncorrected heat of evaporation calculated from the pressures is 6140 cal.

Of considerable interest is the fact that gaseous NO_2Cl decomposes at a measurable rate in the temperature range 100° to 150°. The decomposition reaction is of the first order, and for a given run the rate constants are nicely constant. Variations in the initial pressures lead, however, to variations in the first-order rate constants, as the following table of the results of Schumacher and Sprenger [*Z. phys. Chem.*, **12B,** 115 (1931)] shows.

Table 11

THE RATES OF THERMAL DECOMPOSITION OF $NO_2Cl(g)$

$$NO_2Cl = NO_2 + Cl \quad \text{(slow)}$$
$$NO_2Cl + Cl = NO_2 + Cl_2 \quad \text{(rapid)}$$
$$-\frac{dp_{NO_2Cl}}{dt} = kp_{NO_2Cl}$$

$\overset{\circ}{p}_{NO_2Cl}$ in mm	$k \times 10^3$ in min^{-1}	$\overset{\circ}{p}_{NO_2Cl}$ in mm	$k \times 10^3$ in min^{-1}
100°		140°	
103.4	1.11	11.1	7.22
184.0	1.73	74.7	23.5
291.8	2.63	142.0	36.4
384.0	11.4	252.0	57.1
594.0	13.7	506.0	82.2
130°		150°	
11.4	3.41	11.2	14.2
48.1	7.59	50.5	35.7
102.5	11.3	105.8	62.9
208.0	23.0	152.4	93.2
412.2	34.8		

$p^{\circ}_{NO_2Cl}$ is the initial pressure of $NO_2Cl(g)$ in mm of Hg.
k is expressed in min^{-1}. ΔE (activation) = 20,500 cal.

Not only does k depend upon $\overset{\circ}{p}_{NO_2Cl}$, but it is also determined by the pressure of any added unreactive gas such as CO_2, NO_2, N_2, and others. This effect of pressure on the rate constants is explained by assuming that the rate of decomposition of the excited molecules depends on the distribution of the excitation energy among the vibrational degrees of freedom of the molecules [see Rice and Sickman, *J. Am. Chem. Soc.*, **56,** 1444 (1934), for a discussion of the application of recent theories of reaction rates to the decomposition of NO_2Cl]. Nitryl chloride is not the only substance whose specific rate of decomposition in the gas phase is dependent on the total pressure, but it does show the effect in a more marked degree than most compounds for which experimental data are available.

Nitryl chloride, like the fluoride, dissolves readily in water with the formation of nitric and hydrochloric acids

$$NO_2Cl + H_2O = HCl + HNO_3$$

It is to be expected that nitryl chloride will behave as a powerful oxidizing agent and tend strongly to corrode many metals (for example, Hg). Its molecular structure is not known, and it would be of interest to structural chemists to know whether the molecule is pyramidal in shape with the nitrogen atom at the apex, or planar.

Gordon and Spinks [*Canadian J. Res.*, **18B,** 358 (1940)] have reported the formation of nitryl (or nitroxyl) perchlorate, NO_2ClO_4, when ozone, oxides of nitrogen, and chlorine dioxide are mixed. Air is passed through an ozonizer and then mixed with a stream of ClO_2. A white solid of low vapor pressure is produced which hydrolyzes in water according to the equation

$$NO_2ClO_4 + H_2O = HNO_3 + HClO_4$$

Analyses also established the formula as NO_2ClO_4.

Nitrosyl bisulfate (nitroxyl sulfonic acid; nitrosyl sulfuric acid), $NOHSO_4$

The reaction between ice-cold, fuming nitric acid and sulfur dioxide is

$$HNO_3 + SO_2 = NOHSO_4(s)$$

If the solution is warm, the $NOHSO_4$ may remain dissolved. Nitrosyl bisulfate is formed in two other important reactions; namely

$$N_2O_3(\text{l or g}) + 2H_2SO_4\ (\text{conc.}) = 2NOHSO_4\ (\text{soln. in } H_2SO_4) + H_2O$$

and $N_2O_4(\text{l}) + H_2SO_4\ (78 \text{ to } 82\%) = NOHSO_4 + HNO_3$

The first reaction is reversible; a variant of it is the reaction between concentrated sulfuric acid and $NaNO_2$. The second reaction may be employed for the preparation of solid $NOHSO_4$.

In the lead chamber process for the manufacture of sulfuric acid, sulfur dioxide, water vapor, and NO_2 are caused to react in huge lead-lined chambers.

$$NO_2 + SO_2 + H_2O = NO + H_2SO_4$$

The resulting NO is re-oxidized, or partially so, to NO_2 by the oxygen present, and the NO_2-NO mixture is then absorbed by concentrated H_2SO_4 in a separate (Gay Lussac) chamber or tower. The absorption reaction leads to $NOHSO_4$ in sulfuric acid solution. In still another tower, the Glover tower, sulfur dioxide reacts with the sulfuric acid solution of $NOHSO_4$ according to the equation

$$2NOHSO_4 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$

the NO formed being then oxidized by O_2 to NO_2 in the lead chamber. This NO_2 is absorbed later in the sulfuric acid that trickles downward in the stone or brick-filled Gay Lussac tower. In the proper order, the mixture of SO_2 and O_2 first enters the Glover tower, then passes with the NO and NO_2 to the lead chamber, and finally the spent lead-chamber gases NO, NO_2, and O_2 are passed through the Gay Lussac tower to strip them of the nitrogen oxides. In order to complete the cycle, the $NOHSO_4$-H_2SO_4 mixture formed in the Gay Lussac tower is pumped to the top of the Glover tower, where it then trickles downward over an acid-resisting packing and flows countercurrent to the entering sulfur dioxide-air mixture. The important point to be emphasized is that concentrated H_2SO_4 absorbs NO_2 or N_2O_3 to form $NOHSO_4$, and this in turn reacts with SO_2 to form H_2SO_4 and NO. The cycle is completed by the reaction $NO + \frac{1}{2}O_2 = NO_2$. Sulfuric acid is formed in both the Glover tower (about 15% of the total) and the lead chamber.

$NOHSO_4$ may be obtained as colorless plates or rhombic crystals; but as ordinarily prepared in the laboratory, it is an almost hair-like mass of colorless crystals. The pure substance melts at 73° with slow decomposition, the decomposition product being the anhydride $(NOSO_3)_2O$ (colorless crystals of m.p. 217°, b.p. 360° without decomposition). The anhydride is also formed when NO and SO_3, or SO_2 and N_2O_5, are mixed together. $NOHSO_4$ is stable in dry air, but it absorbs moisture readily and deliquesces eventually; it then decomposes according to the reversible reaction mentioned above; namely,

$$H_2O + 2NOHSO_4 = N_2O_3(NO + NO_2) + 2H_2SO_4$$

This reaction takes place rapidly and completely when $NOHSO_4$ is added to water.

Salts of $NOHSO_4$ have never been prepared; little is known of its acidic properties.

$NOHSO_4(s)$ is more soluble in very concentrated sulfuric acid than in less concentrated acid, as the following table shows [see the excellent

TABLE 12

SOLUBILITY OF $NOHSO_4(s)$ IN CONCENTRATED SULFURIC ACID

(Solubilities are expressed in g of $NOHSO_4$ per 100 g of solution.)

Per Cent H_2SO_4	Temperature (°C)		
	0	20.9	49.6
56.7	—	19.3	35.6
73.1	17.3	27.0	46.0
84.1	30.5	42.4	56.5
90.4	35.1	49.2	61.6
99.8	—	62.0	67.8

paper of Elliott, Kleist, Wilkins, and Webb, *J. Chem. Soc.*, **129,** 1219 (1926); earlier papers on $NOHSO_4$ are Lunge and Weintraub, *Z. angew. Chem.*, **12,** 393, 417 (1899); Weber, *J. prakt. Chem.*, **85,** 423 (1862); Müller, *Lieb. Ann.*, **122,** 1 (1862)].

Solutions of $NOHSO_4$ in concentrated sulfuric acid are said to have been distilled without decomposition. In their oxidizing action, the solutions are much like those of nitric acid in concentrated sulfuric acid.

A number of investigators have suggested structures for $NOHSO_4$. It was thought for some time that there were two structures in equilibrium, namely, $NOHSO_4$ and NO_2HSO_3. The basis for this belief was the supposed formation of both nitro and nitroso compounds with dimethylaniline. However, Sperling [*Dissertation*, Leipsig, 1925, reported in *Z. anorg. Chem.*, **190,** 328 (1930)] and others have shown that pure nitrosyl bisulfate gives only the nitroso compound and that the reported. nitro compound probably came from nitric acid present in the reaction mixture. Nitrosyl perchlorate, prepared by the action of a mixture of NO and NO_2 on strong $HClO_4$ (70% or higher), has been shown [Hantzsch and Berger, *Z. anorg. Chem.*, **190,** 321 (1930)] by its conductance in nitromethane to behave as a highly ionized salt. It was also shown that the nitrogen content in the cathode region increases. This strong evidence for a salt-like structure with the nitrosyl cation is further supported by Raman spectra measurements of Angus and Leckie [*Proc. Roy. Soc.*, **A 149,** 334 (1935); a good summary of previous work on the structure of the nitrosyl compounds is also given]. They examined both $NOClO_4$ and $NOSO_4H$ in the form of crystals and in solution in the respective acids, perchloric and sulfuric. Spectra very similar to that of the corresponding acid were found in each case, but with the addition of a strong line at about 2315 cm^{-1} which was ascribed to the NO^+ ion. X-ray photographs have shown that crystalline $NOClO_4$ and $NOBF_4$ have the same structure as NH_4ClO_4 and NH_4BF_4 [Klinkenberg, *Rec. trav. chim.*, **56,** 749 (1937)].

If a concentrated sulfuric acid solution of $NOHSO_4$, or a nitrate, or a solution of any other nitrosyl compound, is treated with Cu, Hg, Zn, Fe, or other suitable metals, the solutions become blue in color (red with Fe). The colored substance is given the formula NOH_2SO_4 and is called nitrosisulfonic acid [Raschig, *Z. angew. Chem.*, **18,** 1281 (1905); Lunge and Berl, *ibid.*, **19,** 881 (1906)]. It is unstable and decomposes readily with the formation of nitric oxide and sulfuric acid. In the Lunge nitrometer, the blue-colored compound is formed as an intermediate in the reaction

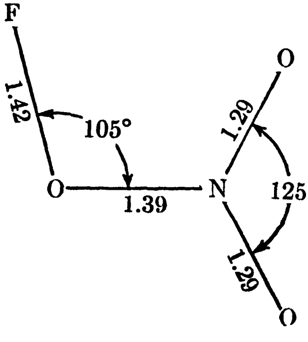
$$8HNO_3 + 3Hg = 2NO + 3Hg(NO_3)_2 + 4H_2O$$

Lunge's method for the determination of nitrogen in nitrates consists in placing a solution of the nitrate in strong sulfuric acid in contact with mercury and measuring the volume of NO evolved. The blue color, as well as the formula given, suggests that NOH_2SO_4 is an "odd" molecule; and if this is the case, the compound is probably paramagnetic.

Fluorine nitrate

It was discovered by Cady that when fluorine is bubbled into nitric acid, a colorless gas is formed which has the formula NO_3F. It was later found that NO_3F could be prepared more conveniently by passing fluorine over solid potassium nitrate [Yost and Beerbower, *J. Am. Chem. Soc.*, **57**, 781 (1935)]. NO_3F gas (b.p. −45.9°, m.p., −175°) explodes when a test tube of it is heated over a Bunsen flame. If fluorine is passed into a test tube containing a few crystals of KNO_3, the tube is soon filled with the colorless gas; and if the tube is then loosely stoppered with a cork stopper and heated a short time over a Bunsen flame, the resulting explosion of the NO_3F will eject the stopper in a lively fashion but will not shatter the tube. NO_3F dissolves to some extent in water and decomposes slowly in the solution to give HF, HNO_3, and O_2. The freshly prepared aqueous solutions are very strong oxidizing agents, being capable, for example, of oxidizing Ag^+ to Ag_2O_3. The slow reactivity with water makes it possible to wash the gas for purposes of purification. Solid NO_3F at liquid-air temperatures is violently and dangerously explosive, little or no shock being sufficient to set it off. In the liquid state, no explosions have been reported. The liquid is colorless when pure, but before purification it may have a slightly yellow color.

The structure of the NO_3F molecule has been determined by the electron-diffraction method [Pauling and Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937)]. As is to be expected, the structure is similar to that ordinarily ascribed to nitric acid; the three oxygen atoms are coplanar with the nitrogen atom. The dimensions shown in the figure are in Ångstrom units.



The Oxyacids of Nitrogen

The known oxyacids of nitrogen are presented in the following list together with a method of preparation for each. In most cases the free acids or their aqueous solutions are unstable; in such cases the formula of a known salt is given in parentheses.

$H_2N_2O_2(Ag_2N_2O_2)$	Hyponitrous	$(NaNO_2 +$ Na amalgam)
$H_2ONNO_2(Na_2ONNO_2)$	Nitrohydroxylamic	$(NH_2OH + CH_3NO_3 +$ NaOH in $CH_3OH)$
$H_2NO_2(Na_2NO_2)$	Hydronitrous or nitroxylic	(Electrolysis of $NaNO_2$ in liquid NH_3)
$HNO_2(NaNO_2)$	Nitrous	$(NaNO_3$ (fused) $+ Pb$; $N_2O_3 + NaOH)$
HNO_3	Nitric	$(NO_2 + O_2 +$ water)

Hyponitrous acid

Free hyponitrous acid, $H_2N_2O_2$, has been prepared by treating an ethereal solution of hydrogen chloride with silver hyponitrite. The reaction is

$$Ag_2N_2O_2(s) + HCl \text{ (in ether)} = AgCl(s) + H_2N_2O_2 \text{ (in ether)}$$

and on evaporating the ether solution, white crystals of $H_2N_2O_2$ are obtained [Hantzsch and Kaufmann, *Lieb. Ann.*, **292**, 323 (1896)]. The free acid decomposes on standing or heating into nitrogen, oxides of nitrogen, and water; the decomposition on heating is often so rapid that the substance explodes. Hyponitrous acid dissolves readily in water, but in solution a moderately rapid decomposition into water and N_2O takes place. Free $H_2N_2O_2$ is also soluble in ether, chloroform, and benzene, but not in ligroin or petroleum ether.

The salts of hyponitrous acid decompose much less rapidly than does the free acid. The relatively insoluble silver hyponitrite, a bright-yellow solid, is ordinarily the starting point for the preparation of pure solutions of the other salts. It is obtained by treating an alkaline solution of the sodium salt with silver nitrate, and the sodium salt in turn is prepared in solution by reducing sodium nitrate or nitrite with sodium amalgam.

The reduction of sodium nitrite to hyponitrite can be brought about as follows: An amalgam containing 25 g of metallic sodium in 140 cc of mercury is added slowly and with shaking to a cooled solution of 25 g $NaNO_2$ in 50 cc of water. After the necessary amount of amalgam has been added, the aqueous mixture is removed from the cooling bath and is shaken for some thirty minutes to an hour to assure that any hydroxylamine present is converted to ammonia. The addition of silver nitrate to a few drops of the reaction mixture followed by enough nitric acid to make it just acid will produce a black precipitate of metallic silver if hydroxylamine is present; hyponitrites do not reduce silver ion under the same conditions. The reaction mixture is decanted from the mercury, and the $Na_2N_2O_2{\cdot}8H_2O$ present is filtered off with asbestos. After trituration with alcohol and filtering, the product may be used at once or it may be further purified by recrystallization from its concentrated solutions [Divers, *J. Chem. Soc.*, **75,** 96 (1899); Weitz and Vollmer, *Ber.*, **57,** 1016 (1924); Partington and Shah, *J. Chem. Soc.*, 2071 (1931)]. The main reaction is

$$2NO_2^- + 4Na + 2H_2O = N_2O_2^= + 4Na^+ + 4OH^-$$

but there are a number of side reactions which yield hydroxylamine, ammonia, and even hydrogen. The reaction mixture soon becomes strongly alkaline as a result of the main and the side reactions. The pentahydrate, $Na_2N_2O_2{\cdot}5H_2O$, can be obtained by crystallization from strong alkaline solutions; the water of crystallization is given off in a vacuum desiccator, and a white, magnesia-like powder results. Both the hydrated and the unhydrated salt are readily soluble in water but not in alcohol. The octahydrate is said to result when an aqueous solution of $Na_2N_2O_2$ is concentrated in a vacuum desiccator containing sulphuric acid. On heating to some 300°, sodium hyponitrite decomposes into nitrogen, nitrous oxide, sodium nitrite, sodium oxide, and other products.

A modification of the above reduction with sodium amalgam has been perfected by Abel and Proisl [*Monatshefte*, **72,** 1 (1938)]. The amalgam is formed by making mercury the cathode in an electrolytic cell containing sodium hydroxide solution as the electrolyte. By mechanical stirring, the amalgam is caused to circulate into an inverted vessel dipping into the mercury and containing sodium nitrite and hydroxide (200 g $NaNO_2$, 50 g NaOH, in 1 liter of solution). Carbon dioxide-free air is used to stir the nitrite solution. From one to two amperes for two days are required to bring about the reduction of 200 g of $NaNO_2$. The strongly alkaline solution in the inverted vessel is removed, rapidly neutralized with nitric acid, and then treated with silver nitrate to precipitate the bright-yellow $Ag_2N_2O_2$. The precipitate is separated by decantation and then thoroughly washed. It is necessary to protect silver hyponitrite from light in order to prevent photochemical decomposition.

The reduction of nitrite to hyponitrite may also be brought about with stannous chloride [Raschig, *Z. anorg. Chem.*, **155,** 225 (1926)], the best yield being obtained when equal volumes of 0.22 m $SnCl_2$ (free from excess HCl) and 0.20 m $NaNO_2$ are mixed at room temperature; the tin is precipitated and removed as hydroxide by the addition of excess sodium acetate. From the resulting filtered solution, after evaporating at 35° under vacuum to one-tenth the original volume, the $H_2N_2O_2$ is extracted with ether. Both hydroxylamine and N_2O are products of the reduction, the yield of $H_2N_2O_2$ being 3% and that of hydroxylamine 7½%.

The hydrolysis of sodium hydroxylamine monosulfonate, $NaHONHSO_3$, in the presence of rather concentrated potassium hydroxide leads to good (60–80%) yields of hyponitrite. The reduction of the salt $K_2N_2O_2SO_3$, which is obtained from the reaction $NO + K_2SO_3$ (in conc. KOH), also produces hyponitrite.

Hyponitrites can also be prepared by the interaction of hydroxylamine, sodium ethylate, and ethyl nitrite. Hydroxylamine hydrochloride is dissolved in an alcoholic (absolute) solution of sodium ethylate and, after cooling and filtering to remove NaCl, the resulting solution is cooled in a freezing mixture, and the ethyl nitrite is distilled directly into it. Sodium hyponitrite precipitates out and is filtered free from the mixture and washed with cold absolute alcohol and ether. The yield is about 13% [Jones and Scott, *J. Am. Chem. Soc.*, **46**, 2172 (1924)]. The main reactions are:

$$NH_2OH{\cdot}HCl + NaC_2H_5O = NH_2OH \text{ (in } C_2H_5OH) + NaCl(s)$$
$$NH_2OH + C_2H_5NO_2 + 2NaC_2H_5O = Na_2N_2O_2(s) + 3C_2H_5OH$$

The doubled formula of the hyponitrite ion $N_2O_2^=$ has been established by freezing-point experiments on aqueous solutions of its salts [see, for example, Divers, *J. Chem. Soc.*, **75**, 122 (1899)].

Aqueous solutions of $Na_2N_2O_2$ are alkaline to litmus, and acid salts of the formula MHN_2O_2 are known. These facts show that hyponitrous acid is weak, and this is shown quantitatively by the ionization constants found by Latimer and Zimmerman [*J. Am. Chem. Soc.*, **61**, 1550 (1939)].

$$\frac{(H^+)(HN_2O_2^-)}{(H_2N_2O_2)} = 9 \times 10^{-8} \text{ at } 25°$$
$$\frac{(H^+)(N_2O_2^=)}{(HN_2O_2^-)} = 1.0 \times 10^{-11} \text{ at } 25°$$

The second ionization constant was also evaluated by Abel and Proisl from the results of reaction-rate measurements, but they obtained the appreciably lower value of 10^{-13}.

Alkaline sodium hyponitrite solutions decompose only slowly at room temperature, but in acid solution the rate of decomposition is rapid, the products of the decomposition in both cases being nitrous oxide and sodium hydroxide.

$$N_2O_2^= + H_2O = N_2O + 2OH^-$$

At 25° or above, the alkaline solutions decompose at a measurable rate, and the rate and the mechanism of the reaction have been thoroughly investigated by Abel and Proisl [*Monatshefte*, **72,** 1 (1938)]. They found that the rate equation is:

$$\frac{d(N_2O)}{dt} = \frac{k(N_2O_2^=)_s}{(OH^-)\{1 + \beta(OH^-)\}}$$

where $(N_2O_2^=)_s$ stands for the total concentration of hyponitrite, and k and β are constants whose values are shown in the table. From the fact that both ionization constants of $H_2N_2O_2$ are small, it follows that both HNO_2^- and $N_2O_2^=$ will be present at appreciable concentrations in the solutions. A chemical analysis of the solutions gives the total concentration of hyponitrite, $(N_2O_2^=)_s$, but the various hyponitrite species present do not, as Abel and Proisl showed, all decompose at the same rate. Since the acid is weak, rapid reversible hydrolysis will occur; accordingly,

Temp. (°C)	k^a	β^a
25	6.0×10^{-5}	2.9
50	4.0×10^{-3}	2.0
55	7.1×10^{-3}	1.3

[a] Concentrations in moles/liter, time in minutes.

$$N_2O_2^= + H_2O = HN_2O_2^- + OH^- \qquad K_1 = \frac{(HN_2O_2^-)(OH^-)}{(N_2O_2^=)}$$

$$HN_2O_2^- + H_2O = H_2N_2O_2 + OH^- \qquad K_2 = \frac{(H_2N_2O_2)(OH^-)}{(HN_2O_2^-)}$$

If the rate-determining step in the decomposition is assumed to be

$$H_2N_2O_2 = N_2O + H_2O$$

that is,

$$\frac{d(N_2O)}{dt} = k'(H_2N_2O_2)$$

then since, effectively,

$$\begin{aligned}(N_2O_2^=)_s &= (N_2O_2^=) + (HN_2O_2^-)\\ &= (H_2N_2O_2)\left[\frac{(OH^-)^2}{k_1k_2} + \frac{(OH^-)}{K_2}\right]\end{aligned}$$

the rate equation takes the form

$$\frac{d(N_2O)}{dt} = \frac{k'(N_2O_2^=)_s}{(OH^-)\left[\dfrac{1}{K_2} + \dfrac{(OH^-)}{K_1K_2}\right]} = \frac{k'K_2(N_2O_2^=)_s}{(OH^-)\left[1 + \dfrac{(OH^-)}{k_1}\right]}$$

If we put

$$k'K_2 = k \qquad \text{and} \qquad \frac{1}{K_1} = \beta$$

3 4 0 6 3

we may finally write

$$\frac{d(\mathrm{N_2O})}{dt} = \frac{k(\mathrm{N_2O_2^=})_{\bullet}}{(\mathrm{OH^-})\{1 + \beta(\mathrm{OH^-})\}}$$

The derived-rate equation based on the assumed mechanism is evidently identical with that found experimentally; hence the mechanism assumed is justified. It is to be noted that $\beta = 1/K_1$; and since K_1 is related to the ionization constant of water and that (the second) of hyponitrous acid, $K_1 = K_w/K_A$, it is clear that K_A may be calculated from β and the known values of K_w [$K_w = 1.0 \times 10^{-14}(25°)$, $5.48 \times 10^{-14}(50°)$, $7.30 \times 10^{-14}(55°)$]; thus, at 25°, $K_A = (\mathrm{H^+})(\mathrm{N_2O_2^=})/(\mathrm{HN_2O_2}) = K_w/K_1 = \beta K_w = 2.9 \times 1.0 \times 10^{-14} = 2.9 \times 10^{-14}$. This value is considerably less than that given above, namely, 1.0×10^{-11}; but, inasmuch as no account has been taken of activity effects, the agreement is reasonably satisfactory. The main features of the mechanism may be regarded as fairly well established.

The hyponitrites are not very reactive toward even strong reducing agents. Sodium amalgam, a very strong and active reducing agent, has little if any effect on solutions of hyponitrites. Indeed, the fact that they are formed by the action of powerful reducing substances on nitrites indicates the rather marked lack of reactivity toward further reduction. If, for analytical purposes, it is desired to convert the hyponitrite to ammonia, it is necessary first to oxidize it to the nitrate stage.

Aqueous solutions of hyponitrous acid and the hyponitrites are strong reducing agents. They are oxidized by the halogens to nitrates. Permanganate in alkaline solution oxidizes hyponitrite ion with moderate rapidity to nitrite ion; if, after some fifteen minutes, excess permanganate is added to the alkaline solution, and if the mixture is then made acid, complete oxidation to nitrate ion is brought about. These reactions form the basis for an analytical procedure in which hyponitrite is determined volumetrically [Thum, *Monatshefte*, **14**, 297 (1893)]. In alkaline solution the reaction between permanganate and hyponitrite is not extremely rapid; in acid solution side reactions render the direct oxidation unsuitable for analytical purposes.

The oxidation of aqueous solutions of $\mathrm{CaN_2O_2 \cdot 4H_2O}$ with bromine was used by Berthelot as a means for determining the heat of formation of hyponitrous acid and hyponitrite ion [see Bichowsky and Rossini, *Thermochemistry*]. More recently, Latimer and Zimmerman [*J. Am. Chem. Soc.*, **61**, 1550 (1939)] have redetermined the heat of formation of $\mathrm{H_2N_2O_2}$ (aq), and they have also made estimates of the entropy changes attending the formation of the hyponitrite ions. Their results are summarized in the following equations:

	ΔH°_{298} (cal)	ΔF°_{298} (cal)
$H_2(g) + N_2(g) + O_2(g) = H_2N_2O_2(aq)$	−11,300	11,000
$N_2(g) + O_2(g) + \frac{1}{2}H_2(g) + E^- = HN_2O_2^-$	−7,000	20,400
$N_2(g) + O_2(g) + 2E^- = N_2O_2^=$	−200	35,400

It is often asserted that nitrous oxide, N_2O, is not the anhydride of hyponitrous acid. In the sense that an easily measurable quantity of the acid does not result when N_2O reacts with water, the assertion is true. From the point of view of chemical equilibria, one must say that the reaction has such a great tendency to go in the reverse direction that the concentration of $H_2N_2O_2$ is never large. The free-energy equation is

$$N_2O(g) + H_2O(l) = H_2N_2O_2(aq), \qquad \Delta F^\circ_{298} = 42{,}760 \text{ cal}$$

and it is an easy calculation to show that, for a 0.001 m solution of $H_2N_2O_2$, the equilibrium pressure of N_2O would be about 10^{27} atmospheres. Even if the reaction proceeds as written, the pressure of N_2O required to yield a measurable concentration of $H_2N_2O_2$ is much too high to be attainable in practice.

Concerning the structure of hyponitrite ion, little of an exact nature is known. It seems reasonable to suppose that the two nitrogens are joined together, since in N_2O this has been found to be the case. Sufficient information is not available to permit of a statement regarding the angle made by the two end oxygens with the N—N bond.

Nitrohydroxylamic acid, H_2ONNO_2

The free acid is not known, but the sodium and other metal salts have been prepared. To prepare the sodium salt, a concentrated solution of sodium ethylate in absolute alcohol is mixed with a warm, saturated solution of hydroxylamine hydrochloride in alcohol. Sodium chloride precipitates from this mixture and is filtered off, and ethyl nitrate is added to the filtrate; on cooling this mixture, $Na_2N_2O_3$ separates out as a white powder. The salt is readily soluble in water but not in alcohol. On the addition of acid to the solutions of $Na_2N_2O_3$, decomposition sets in at once, the products being NO and water. Aqueous solutions of the salt are alkaline, a fact which shows that $HN_2O_3^-$ and doubtless $H_2N_2O_3$ also are weak acids. On heating, solutions of the sodium salt decompose to give nitrous oxide and nitrite ion, and it has been assumed that the hypothetical HNO is an intermediate in the decomposition [Angeli, *Gazz.*, **33 II,** 245 (1903)]. The addition of alkaline earth chlorides to solutions of $Na_2N_2O_3$ results in precipitates of the type BaN_2O_3. With soluble lead and cadmium salts, precipitates are also formed (PbN_2O_3 is yellowish, CdN_2O_3 is white); but with silver and mercury salts, reduction to the metals sets in shortly after the formation of the insoluble nitrohydroxylamites [Angeli, *Gazz.*, **26 II,** 19 (1896)].

Aqueous solutions of $Na_2N_2O_3$ are readily oxidized. Atmospheric oxygen carries the oxidation to the nitrite stage, but permanganate brings about oxidation to nitrate ion if the initially alkaline mixture is made acid. The first step, in alkaline solution, leads to nitrite, and this in acid solution is oxidized to nitrate by permanganate. The reactions with iodine and ferric ion yield both nitrite and nitric oxide [Cambi, *Gazz.*, **59,** 780 (1929)]. With reducing agents, hyponitrous acid is assumed to be formed in an intermediate step [Nichols and Morse, *J. Phys. Chem.*, **35,** 1250 (1931)], and this in turn would decompose into N_2O. The experiments on the action of reducing agents were not carried out on $N_2O_3^{=}$ itself but on aqueous solutions of nitric oxide, and it was assumed that these solutions contained $H_2N_2O_3$ as the result of an hydrolysis of NO.

Hydronitrous acid

Only the sodium salt of this acid is known, and it is prepared by the electrolysis of liquid ammonia solutions of sodium nitrite [Maxted, *J. Chem. Soc.*, **111,** 1016 (1917), Zintl and Kohn, *Ber.*, **61,** 189 (1928)] or by treating liquid ammonia solutions of metallic sodium with $NaNO_2$. The end point in the latter reaction is reached when the blue color of dissolved sodium has disappeared. Sodium hydronitrite is not very soluble in liquid ammonia and forms a yellow precipitate from which the ammonia can be readily evaporated. The formula of the brilliant yellow-colored Na_2NO_2 suggests, if the compound is monomeric, that it should be paramagnetic, since the total number of valence electrons is odd. In moist air or water, the compound explodes and hydrogen is formed. When protected from moisture and oxygen, the dry salt may be heated to 100° without decomposition, but above this temperature violent decomposition to Na_2O, N_2, $NaNO_2$, and $NaNO_3$ takes place. Na_2NO_2 reacts with cxygen to form a peroxide.

Nitrous acid, HNO_2

Nitrous acid appears to exist in the vapor state, and aqueous solutions of it may be prepared without difficulty. Although a large number of reactions lead to its formation, the simplest method of preparing it consists in the addition of a strong acid to a solution of a soluble nitrite. Thus, a solution of $Ba(NO_2)_2$ when treated with an equivalent amount of H_2SO_4 gives, because of the insolubility of $BaSO_4$, a solution of the weak acid HNO_2. When the presence of metal ions is of no consequence, the mere addition of a strong acid to the solution of a nitrite, $NaNO_2$, for example, yields a solution containing nitrous acid.

Nitrous acid solutions may also be prepared by causing gaseous or liquid N_2O_3 to dissolve in water. Such solutions will, in general, contain nitric acid and the dissolved oxides NO and N_2O_4 as well; with ice water, the concentration of HNO_2 in dilute solutions will be considerably greater than that of nitric acid. As has been noted in a previous section, an equal molal mixture of NO and NO_2 will condense to a blue or greenish-blue liquid consisting, for the most part, of N_2O_3 together with some dissolved NO and N_2O_4. When water is added to this liquid, two layers are formed, an aqueous upper layer which is blue in color if the concentration of N_2O_3 is greater than some 20% (in long columns, the blue color is observed with 5% N_2O_3 solutions), and a lower, very deep blue layer consisting principally of N_2O_3. On heating the H_2O—N_2O_3(l) mixture in closed tubes, the two phases can be made to disappear, the temperature of complete miscibility depending on the composition of the mixture. If the two-phase mixture is cooled sufficiently, ice separates out, the temperature of the freezing point depending on the composition of the mixture. In Fig. 13 are shown both the freezing points and the points of complete miscibility for H_2O—N_2O_3 mixtures for the complete range of compositions [Lowry and Lemon, *J. Chem. Soc.*, 1 (1936)]. The diagram shows, for example, that an equimolal mixture of N_2O_3 and water will, above 55°, consist of a solution of N_2O_3 in water; that is, it will be a strong aqueous solution of nitrous acid, HNO_2.

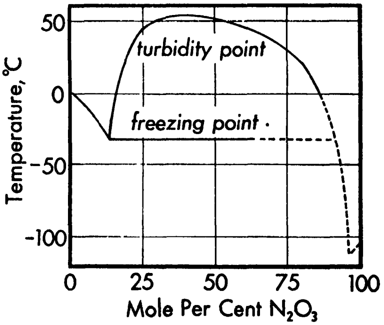


Fig. 13. **Phase Diagram of the System N_2O_3—H_2O.** The turbidity point is the temperature at which two liquid phases separate; the freezing point is the temperature at which ice separates from the solution.

When a strong acid is added to a solution of sodium or other nitrite, nitric oxide gas, NO, is evolved. The equation for this important reaction is

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O$$

and the reaction is reversible. The rate of decomposition is measurable, as is also the rate of the reverse reaction. The first effect of adding the strong acid is to bring about the formation of the weak acid HNO_2, the extent of whose ionization is calculable from the following mass-action expression [Schumann, *Ber.*, **33**, 527 (1900); Klemenc and Hayek, *Monatshefte*, **54**, 407 (1929)].

$$HNO_2 = H^+ + NO_2^- \qquad \frac{(H^+)(NO_2^-)}{(HNO_2)} = 6.0 \times 10^{-4} \text{ at } 30°$$

The nitrous acid then decomposes, at a rate that is dependent on the concentration of nitrous acid and the partial pressure of NO. In a series of very thorough investigations, Abel and his coworkers [see, for example, *Z. phys. Chem.*, **148,** 337 (1930) and also Bray, *Chem. Rev.*, **10,** 161 (1932)] have found that if the partial pressure of NO above solutions of HNO_2 is kept constant, then, at the beginning of the decomposition,

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O$$

$$-\frac{d(HNO_2)}{dt} = \frac{k_1(HNO_2)^4}{P^2_{NO}} \qquad k_1 = 46 \text{ at } 25°$$

and at the beginning of the reverse reaction

$$\frac{d(HNO_2)}{dt} = k_2(HNO_2)(H^+)(NO_3^-) \qquad k_2 = 1.6 \text{ at } 25°$$

the concentrations being expressed in moles/l, the pressures P_{NO} in atmospheres, and the time in minutes. At other temperatures, the following values of k_1, in the same units, were found.

Temp., t(°C)	0	10	25	40	60
k_1	0.602	3.63	46	525	5130

The temperature coefficient of k_1,

$$\frac{k_{1(t+10°)}}{k_{1(t)}}$$

is 6.7 at 5° and 3.2 at 50°.

When either the forward or reverse reaction has proceeded beyond the initial stage, then

$$\frac{d(HNO_2)}{dt} = k_2(HNO_2)(H^+)(NO_3^-) - \frac{k_1(HNO_2)^4}{P^2_{NO}}$$

and at equilibrium $d(HNO_2)/dt = 0$ and $k_1/k_2 = K$, the equilibrium constant. The following values of $K = (H^+)(NO_3^-)P^2_{NO}/(HNO_2)^3$ with concentrations in moles per liter and pressures in atmospheres have been obtained from both rate and equilibrium measurements.

Temp. (°C)	12.5	15	24.9	30
K	13.3	14.1	28.7	39.6

$\Delta H° = 11{,}900$ cal

The mechanism of the forward (decomposition) and reverse reaction proposed and justified by Abel is included in the following reactions.

$$\begin{array}{l} \text{Forward} \\ \text{Reaction} \end{array}\left\{\begin{array}{lr} 4HNO_2 = N_2O_4 + 2NO + 2H_2O, \text{ rapid and reversible} & (1) \\ N_2O_4 + H_2O = HNO_2 + H^+ + NO_3^-, \text{ rate-determining} & \\ \qquad\qquad\qquad\qquad \text{step } (k = 1 \times 10^7 & \\ \qquad\qquad\qquad\qquad \text{at } 25^\circ) & (2) \end{array}\right.$$

$$\begin{array}{l} \text{Reverse} \\ \text{Reaction} \end{array}\left\{\begin{array}{lr} HNO_2 + H^+ + NO_3^- = N_2O_4 + H_2O, \text{ rate-determining} & \\ \qquad\qquad\qquad\qquad \text{step} & (3) \\ N_2O_4 + 2NO + 2H_2O = 4HNO_2, \text{ rapid-follow reaction} & (4) \end{array}\right.$$

Reaction (2) is assumed to be much slower than (4), and this is in agreement with the well-known fact that N_2O_4 dissolves much less rapidly in water or alkali than does the mixture $N_2O_4 + 2NO$. In fact, when $N_2O_4(g)$ dissolves in alkali, a mixture of nitrite and nitrate ions results; but when a mixture whose composition corresponds to N_2O_3 dissolves in alkali, a solution containing much nitrite but very little nitrate is formed, in spite of the fact that the equilibrium pressure of $N_2O_3(g)$ is much smaller than that of N_2O_4 or NO_2 in the N_2O_3 mixture. The study made by Abel has thrown considerable light on a set of reactions of great importance both in pure chemistry and in chemical technology.

The salts of nitrous acid are of great importance in the manufacture of dyes and a variety of other substances. Accordingly, the methods of manufacture have received considerable attention. The starting materials consist of (1) Chile saltpeter, $NaNO_3$, or (2) the nitrogen oxides obtained in the arc process ($N_2 + O_2$) or by the oxidation of ammonia with atmospheric oxygen in the presence of a catalyst. When sodium nitrate is the starting material, it is usually fused alone (m.p. 308°) or together with NaOH or Na_2CO_3 in the presence of a reducing agent. A number of reducing agents have been tried; for laboratory purposes metallic lead serves nicely, but for large-scale operations a cheaper substance is necessary. The following list of reducing agents together with the practically obtainable yields from them will give some idea of the directions that the search for a solution of the problem has taken:

$$NaNO_3(l) + R = NaNO_2(l) + RO$$

R	Yield from $NaNO_3$(%)	*R*	Yield from $NaNO_3$(%)
S	56	FeO	83
Pyrite, FeS_2	66.7	Wood Charcoal	25
FeS	63	Coke[a]	77
Fe[a]	86.4		

[a] A fused mixture of $NaNO_3$ and NaOH is used.

It is evident that metallic iron and coke have over-all advantages over the other substances listed. This list is not an exhaustive one; SO_2, CO, and several other reducing agents have been tried or used at one time or another.

When the reduction reaction is complete, the mixture consists of $NaNO_2(l)$ (m.p. 271°), NaOH, and the oxidized form of the reducing agent, if this is not a gas, together with unreacted material. After cooling, the mixture is dissolved in water, and the salts present are then crystallized from the solution. Sodium nitrite is very soluble in water (72 g at 0° and 163 g at 100°, per 100 g water) and may be the last salt recovered.

In the second method for the manufacture of nitrites, the oxides of nitrogen are made to dissolve in a solution of alkali or they are absorbed by a solid hydroxide. Since a mixture of NO and NO_2, corresponding to the composition of N_2O_3, dissolves to form much nitrite and but little nitrate, the mixed gases from the arc process or the ammonia oxidation process are heated to such a temperature (from 150° to 300°) that the reversible reaction $NO + \frac{1}{2}O_2 = NO_2$ results in an almost equimolal mixture of NO and NO_2 (a slight excess of NO proves to be advantageous). The absorbing solution of NaOH, KOH, Na_2CO_3, or $Ca(OH)_2$ is eventually subjected to recrystallization to recover the nitrite salts.

The alkali and alkaline earth nitrites, nearly colorless or yellow, are quite soluble in water but much less so in alcohol and ether. They are also very soluble in liquid ammonia. The heavy metal nitrites are often slightly soluble in water. The following table of solubilities shows these facts quantitatively.

TABLE 13
SOLUBILITIES OF NITRITES

Substance	Solubility, Moles of Unhydrated Salt/1000 g H_2O		
	−5–0°	20–40°	60–100°
$LiNO_2 \cdot H_2O$	13.6 (0°)	24.0 (40°)	72.8 ($\frac{1}{2}H_2O$ 90°)
$NaNO_2$	10.48 (0°)	11.98 (20°)	23.5 (100°)
KNO_2	32.9 (0°)	35.5 (20°)	
$RbNO_2$	V. Sol.		
$CsNO_2$	V. Sol.		
$Ca(NO_2)_2 \cdot 4H_2O$	4.68 (0°)	6.66 (30°)	18.1 ($1H_2O$ 90°)
$Sr(NO_2)_2 \cdot H_2O$	2.75 (−5°)	4.26 (35°)	7.90 (100°)
$Ba(NO_2)_2 \cdot H_2O$	2 39 (0°)	3.49 (30°)	13.9 (100°)
$AgNO_2$	0.0102 (0°)	.0270 (25°)	.0897 (60°)

$LiNO_2$ is very soluble in alcohol; the remaining salts in the list are only slightly soluble. Liquid ammonia dissolves many nitrites readily.

The alkali and alkaline earth nitrites are quite stable toward heat, most of them melting with little or no decomposition.

Silver nitrite suspended in water decomposes reversibly according to the equation [Abegg and Pick, *Z. anorg. Chem.*, **51,** 1 (1906); Lewis and Adams, *J. Am. Chem. Soc.*, **37,** 2308 (1915)]:

$$2AgNO_2(s) = Ag^+ + NO_3^- + Ag(s) + NO(g)$$

At room temperatures the reaction is very slow, but at 55° equilibrium is established in a few days, the pressure of NO being 4.28 atmospheres when the concentration of $AgNO_3$ is 0.179 m. At 100° and 1.10 m $AgNO_3$, $P_{NO} = 8.35$ atm. The extrapolated pressure of NO for 25° and $(AgNO_3) = 0.179$ m is 0.162 atm. When the activity of the silver nitrate is taken into account, it is found that

$$2AgNO_2(s) = Ag^+ + NO_3^- + Ag(s) + NO(g)$$
$$\Delta F^\circ_{298} = 3600 \text{ cal}, \qquad \Delta H^\circ = 21{,}200 \text{ cal}$$

When silver nitrite is freshly precipitated, it has a faint yellow color and a curdy appearance. With time, and especially on heating, the precipitate suspended in water becomes dark in color as a result of the silver formed in the above reaction. The dry salt also decomposes on moderate heating to give silver nitrate and nitric oxide, and a careful study of the equilibrium has been made by Randall, Manov, and Brown [*J. Am. Chem. Soc.*, **60,** 694 (1938)]. They find that for the reaction

$$2AgNO_2(s) = Ag(s) + AgNO_3(s) + NO(g)$$
$$\Delta F^\circ_T = 14{,}775 + 6.95T \log_e T - 0.00694T^2 - 0.00000091T^3 - 75.147T$$

or the temperature range 350–450°K.

$$\Delta F^\circ_{298} = 3{,}537 \text{ cal}, \qquad \Delta H^\circ_{298} = 13{,}368 \text{ cal}, \qquad \Delta S^\circ_{298} = 32.98 \text{ cal/deg}$$

Nitrites are formed in an interesting reaction between the alkali and alkaline earth hydroxides and nitric oxide [Barnes, *J. Chem. Soc.*, **133,** 2605 (1931)]:

$$2MOH(s) + 4NO(g) = 2MNO_2(s) + N_2O + H_2O$$

At room temperature the reaction requires, for completion, years with LiOH, months with NaOH, days with KOH, and hours with RbOH and CsOH. At 250° the reactions are much more rapid, but the products change also as a result of the catalytic decomposition of the N_2O formed. The side reaction, which at higher temperatures becomes the predominant one, is

$$4MOH(l) + 6NO(g) = N_2(g) + MNO_2(s) + 2H_2O$$

Nitrous acid and the nitrites act both as oxidizing and as reducing agents. With permanganate there is no reaction in neutral or alkaline solution, but on acidifying the mixture quantitative oxidation to nitrate takes place. Chlorine, bromine, and iodine also oxidize nitrous acid solutions to nitrate. With chlorine the reaction is rapid, and with bromine it is fairly rapid. The reaction between aqueous iodine and nitrite ion is measurably slow, and the rate in buffered solutions ($pH = 6$ to 7) has been studied by Durrant, Griffith, and McKeown [*Trans. Faraday Soc.*, **32**, 999 (1936)]. The net reaction is

$$NO_2^- + I_2 + H_2O = NO_3^- + 2I^- + 2H^+$$

and with phosphate buffers with $(Na_2HPO_4)/(KH_2PO_4) = 0.05/0.2$ to $0.2/0.02$, the experimentally determined rate equation is

$$-\frac{d(\Sigma I_2)}{dt} = \frac{k(NO_2^-)(\Sigma I_2)}{\left\{K + (I^-)\left(\frac{A(I^-)^2}{(NO_2^-)} + 1\right)\right\}}$$

$$K = \frac{(I^-)(I_2)}{(I_3^-)}$$

Representative results for the constants are shown in the table; concentrations are expressed in moles per liter and the time in minutes.

Table 14

RATE CONSTANTS FOR THE OXIDATION OF NITRITE ION BY IODINE

t(°C)	Ionic Strength (moles/liter)	A	$k \times 10^5$	k/K
40	2.7	—	2.94	0.0159
50	0.7	153.5	28.4	.126
	2.7	160.7	13.8	.0612
60	0.7	145.7	115.4	.444
	2.7	140.2	56.6	.2175

More than one mechanism can be set down which is in accord with the empirical rate equation, but one that appears to have features applicable to other reactions is expressed by the following equations.

$$NO_2^- + I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + I^- + I \qquad \text{(rapid)}$$

$$NO_2^- + I \underset{k_4}{\overset{k_3}{\rightleftharpoons}} NO_2 + I^- \qquad \text{(very rapid)}$$

$$2NO_2 + H_2O \overset{k_5}{=} HNO_2 + H^+ + NO_3^- \qquad \text{(slow)}$$

It is not difficult to show that the rapid reversible reactions and the requirements of a steady state with respect to the formation and disappearance of I and NO_2 imply the relation

$$k_1k_3(NO_2^-)^2(I_2) = k_2k_4(NO_2)^2(I^-)^2 + k_3k_5(NO_2^-)(NO_2)^2 + k_2k_5(NO_2)^3(I^-)$$

The last term on the right may be neglected, since k_5 is small compared to the other rate constants, and by hypothesis $k_2 < k_3$. From the rate equation for the slow step

$$-\frac{d(\Sigma I_2)}{dt} = k_5(NO_2)^2$$

and the steady-state relation, it follows that

$$-\frac{d(\Sigma I_2)}{dt} = \frac{k_1(NO_2^-)(I_2)}{1 + \frac{k_2k_4}{k_3k_5}\frac{(I^-)^2}{(NO_2^-)}} = \frac{k_1K(NO_2^-)(\Sigma I_2)}{\{K + (I^-)\}\left\{1 + A\frac{(I^-)^2}{(NO_2^-)}\right\}}$$

where

$$A = \frac{k_2k_4}{k_3k_5}$$

and $k = k_1K$. The temperature coefficient of $k_1 = k/K$ leads to an activation energy of 27,000 cal for the reaction $NO_2^- + I_2 = NO_2 + I^- + I$.

The investigation of this reaction had to be made in the rather narrow range of acid concentrations of $pH = 6$ to 7, since at higher acidities decomposition of HNO_2 sets in, and at lower acidities the hydrolysis of iodine to iodate takes place at an appreciable rate.

On electrolysis alkaline solutions of nitrite are readily oxidized to nitrate at the anode; the rate of anodic oxidation is slower in acid solutions. Hydriodic acid acts as a reducing agent toward nitrous acid solutions, the reaction products being iodine and nitric oxide. Hydrogen peroxide appears to form with acid solutions of nitrites a yellow peroxynitrite $N_2O_6^-$ (thought by some to be identical with the compound resulting from the action of ozone on hydrazoic acid solutions). In acid solution hydrogen peroxide oxidizes nitrous to nitric acid at a measurable rate; in dilute mixtures of HNO_2 (0.0003 − .0009 m) and NO_2^-, the rate equation is [Shilow, Rybakow, and Pal, *Izvestija Ivanovo-Voznesenskogo Politechn. Inst.* (Russia), **15**, 85 (1930); *Chem. Zent.*, **II**, 377 (1931)],

$$H_2O_2 + HNO_2 = NO_3^- + H_2O + H^+$$

$$-\frac{d(H_2O_2)}{dt} = k_1(H_2O_2)(HNO_2)^2 + k_2\frac{(NO_3^-)(H_2O_2)(HNO_2)^4}{(NO_2^-)}$$

$$k_1 = 5.7 \times 10^3, \qquad k_2 = 3.7 \times 10^9 \text{ at } 20^\circ$$

Time is expressed in minutes, concentrations in moles per liter. In the presence of excess acid the mechanism of the reaction changes somewhat, and this rate equation is then no longer valid.

The effect of reducing agents on nitrous acid and nitrites is a function of the agent, of acidity, and of temperature. Thus in cold, neutral, or faintly acid solution sulfite reduces nitrite to hydroxylamine disulfonate, but at room temperature amine sulfonates or nitric oxide are reduction products. Ferrous and titanous ions reduce HNO_2 to NO; with stannous ion nitrous oxide is the principal product, but some hyponitrous acid is formed as well as small amounts of hydroxylamine and ammonia. Very strong reducing agents, such as sodium amalgam, can effect the reduction to hyponitrite; in liquid ammonia solution the nitrites are reduced to hydronitrites by metallic sodium.

Some of the reactions of nitrous acid with reducing agents have been studied with care, such being the case, for example, with arsenious acid. Abel, Schmid, and Weiss investigated this reaction under equilibrium conditions in the reaction leading to the decomposition of nitrous acid [*Z. phys. Chem.*, **147**, 76 (1930)]:

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O$$

The rate equation for the oxidation of arsenious acid then takes the form

$$H_3AsO_3 + 2HNO_2 = H_3AsO_4 + 2NO + H_2O$$

$$\frac{d(H_3AsO_4)}{dt} = k(H_3AsO_3)(HNO_2)^2$$

$$k = 5.75 \times 10^{-3} \text{ at } 25^\circ \text{ (time in minutes, conc. in moles/liter)}$$

A mechanism that is in accord with this equation is

$$2HNO_2 = N_2O_3 + H_2O \qquad \text{(rapid and reversible)}$$

$$N_2O_3 + H_3AsO_3 = H_3AsO_4 + 2NO \quad \text{(rate-determining step)}$$

A large number of reactions involving the oxidation or reduction of nitrites have not been subjected to detailed study, but they exhibit the characteristics of the reactivity of nitrites. Thus aqueous mixtures of $NaNO_2$ and NaN_3 react with a lively evolution of N_2O and N_2 when acidified with acetic acid [Sommer and Pincas, *Ber.*, **48**, 2096 (1915)].

$$HN_3 + HNO_2 = N_2O + N_2 + H_2O$$

Hydroxylamine sulfate solutions react rapidly with nitrous acid with the formation of N_2O and water. Hydrogen sulfide reduces HNO_2 to NO with the formation of elementary sulfur. On the other hand, in a buffer solution of sodium bicarbonate hydrogen sulfide is oxidized to sulfur, but the nitrite is, for the most part, reduced to ammonia. In unbuffered solutions of alkali nitrite, the reaction proceeds nearly quantitatively according to the equation

$$2NO_2^- + 4H_2S = S_2O_3^= + 2S + 2NH_3 + H_2O$$

Thiosulfate reacts readily with nitrous acid solutions to give nitric oxide, hexa- and tetrathionate, and sulfurous and sulfuric acids. Amine sulfonic acid (sulfamic acid), NH_2SO_3H, reacts rapidly and smoothly with nitrous acid to yield nitrogen and sulfuric acid.

$$NH_2SO_3^- + HNO_2 = N_2 + SO_4^= + H^+ + H_2O$$

Of interest for the purposes of quantitative analysis is the reaction between nitrous acid and silver bromate; namely,

$$Ag^+ + BrO_3^- + 3HNO_2 = 3H^+ + 3NO_3^- + AgBr(s)$$

the resulting silver bromide being filtered off and weighed. The silver bromate-alkali nitrite mixture in solution is acidified with acetic acid to bring about the reaction.

A very familiar reaction is the decomposition of aqueous ammonium nitrite solutions according to the equation

$$NH_4^+ + NO_2^- = N_2 + 2H_2O$$

In addition small amounts of nitric oxide and nitric acid are produced through side reactions. The rate of evolution of nitrogen depends on the temperature and acidity of the solution. In the presence of a small amount of added nitric acid and a constant pressure of NO (to prevent decomposition of HNO_2 by the reversible reaction $3HNO_2 + H^+ = NO_3^- + 2NO + H_2O$), the rate of evolution of nitrogen in moles/min is expressed by the equation

$$\frac{d(N_2)}{dt} = k_\mu(NH_4^+)(NO_2^-)(HNO_2) \tag{1}$$

$k_\mu = 0.26$ to 0.17 at 25° for ionic strengths, μ, of 0.2 to 3.0 m.

The time unit is minutes, and concentrations are in moles/liter.

In the absence of added acid, and with *equivalent amounts* of NH_4^+ and NO_2^-, the rate equation takes the apparently different form

$$\frac{d(N_2)}{dt} = k[NH_4NO_2]_s^3 \tag{2}$$

but when the rapid reversible hydrolytic reaction

$$NH_4^+ + NO_2^- + H_2O = NH_4OH + HNO_2$$

is taken into account, it is evident that, since $(NH_4OH)(HNO_2) = (HNO_2)^2 = K(NH_4^+)(NO_2^-) = K[NH_4NO_2]_s^2$, where $[NH_4NO_2]_s$ means the concentration of ammonium nitrite without taking into consideration its ionization, the rate equation (2) reduces to (1) with $k = k_\mu\sqrt{K}$ [Abel, Schmid, and Schafranik, *Z. phys. Chem.*, Bodenstein Festband, 510 (1931)]. The mechanism of the decomposition appears to be given by the following reactions:

$$NH_4^+ + NO_2^- = NH_4NO_2 \qquad \text{(rapid and reversible)}$$
$$NH_4NO_2 + HNO_2 = NH_4NO_2{\cdot}HNO_2 \qquad \text{(rate-determining formation of intermediate)}$$
$$NH_4^+ + NH_4NO_2{\cdot}HNO_2 = 2N_2 + 2H_2O + H^+ \qquad \text{(rapid, irreversible)}$$
$$NO_2^- + H^+ = HNO_2 \qquad \text{(rapid, reversible)}$$

Between 15° and 35° the temperature coefficient of the reaction is normal and has the value

$$\frac{k_{t+10}}{k_t} = 2.9$$

Of the equilibrium physical properties of nitrous acid and the nitrites it will suffice to discuss the vapor pressure of HNO_2 above its solutions. It has been known for some time that a gaseous mixture of NO, NO_2, and H_2O shows some absorption bands different from those of any of its components, including N_2O_3 and N_2O_4. These bands have been ascribed to $HNO_2(g)$, and the partial vapor-pressure measurements of Abel and Neusser [*Monatshefte*, **54**, 855 (1929)] confirm this view. By bubbling NO through aqueous mixtures containing HNO_2, HNO_3, KNO_3, and H_2SO_4 in various proportions, and taking account of all nitrogen compounds present in the vapor phase, Abel and Neusser arrived at the following smoothed values for the constants in Henry's law for nitrous acid.

TABLE 15

THE RATIOS $P_{HNO_2}/(HNO_2)$ FOR NITROUS ACID SOLUTIONS AT 25°

$k' = P_{HNO_2}/(HNO_2)$, pressures in atmospheres, concentrations in moles/liter

$k' = \gamma\, k$; k, a constant, $= 0.0305$

Ionic Strength (moles/liter)	$k' \times 10^4$	Activity Coefficient γ of HNO_2 (aq)
0.4	312	1.03
1.3	332	1.09
1.4	336	1.10
1.9	345	1.13
2.5	357	1.17
2.9	363	1.19
4.8	393	1.29
5.0	396	1.30
7.0	424	1.39

The fact that the k' are fairly constant and increase slowly with the ionic strength is satisfactory evidence for the existence of HNO_2 in the vapor phase. For a solution of ionic strength 0.4 m and 0.1 m in HNO_2, $P_{HNO_2} = 3.12 \times 10^{-3}$ atm or 2.37 mm. In order that this pressure of

HNO_2 may persist, it is necessary that the concentration of HNO_2 remain constant, and to attain this the solution must contain HNO_3 and be saturated with NO at a pressure such that equilibrium with 0.1 m HNO_2 is attained in the reversible reaction

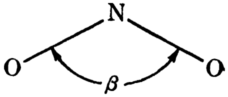
$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O$$

It has been noted above that nitrous acid is weak. Conductivity measurements are ordinarily used to determine the ionization constants, and, from the discussion already given regarding the stability of HNO_2, it is evident that the experiments are attended with difficulties. Klemenc and Hayek [*Monatshefte*, **54**, 407 (1929)] have attained somewhat better accuracy in the measurements than previous investigators, and their results are presented here.

$$K = \frac{(H^+)(NO_2^-)}{(HNO_2)}$$

t(°C).................	0	12.5	30
$K \times 10^4$.....	3 2 ± 0.3	4.6 ± 0.4	6.0 ± 0 6

The structure of the nitrite ion has been a subject of speculation almost since the discovery of the substance. X-ray crystal structure studies on nitrites and analysis of the Raman spectrum of $NaNO_2$ solutions suffice to establish the triangular configuration of the ion.



N—O distance 1.13 Å
β = 120–130°

The N—O distance of 1.13 Å is essentially equal to that found in nitrosyl chloride, NOCl; accordingly, the bonds must be of the same character in both substances. The extra pair of electrons are pictured as resonating from one N—O bond to the other, and the bonds are, on the average, stronger than the normal, single N—O bond and not quite as strong as a double bond.

The Raman spectrum of NO_2^- shows the following lines [Langseth and Walles, *Z. phys. Chem.*, **27**, 209 (1934)]:

Line	Frequency, cm^{-1}	Intensity (relative at 15°)	Polarization, ρ
A	1331.3 ± 1	12.9 (sharp)	0.43
B	1240 ± 2	2.4 (broad)	0.84 ($\frac{6}{7}$)
C	813 2	1.0 (sharp)	0.21

These results are in accord with a triangular configuration for NO_2^- since the selection rules permit three lines (corresponding to the three nondegenerate modes of vibration) in the Raman spectrum; only one (fundamental) line would be permitted for a linear symmetrical model O—N—O. The intense line A is due to the symmetrical stretching mode of vibration, while B must arise from the antisymmetrical mode, since $\rho = \frac{6}{7}$.

The Fixation of Nitrogen and Nitric Acid

Fixation of nitrogen

Elementary nitrogen is not very reactive under ordinary conditions, and it combines at an appreciable rate with only a few substances at ordinary temperatures. At higher temperatures it combines readily with some metals, for example, lithium, calcium, magnesium, and silicon; but since these metals are costly to prepare, they do not present economically practical intermediates for nitrogen fixation. Since combined nitrogen is absolutely essential for the maintenance of life and growth of animals and most plants, and since many plants act to deplete the nitrogen content of the soil, it is necessary either to manufacture and apply nitrogen compounds to the soil, or to plant, at least periodically, those plants which are capable with the help of certain bacteria of fixing nitrogen. Some organisms, known as *nonsymbiotic bacteria*, are capable of absorbing (fixing) nitrogen directly, but they do not serve as the most important source; the nitrogen so fixed does not become available to plants until the organisms die. Another class of bacteria, *symbiotic*, is capable of bringing about nitrogen fixation when aided in the task by certain plants which act as hosts to the bacteria. The nitrogen fixed by nonsymbiotic organisms amounts to as much as 35 pounds per acre annually, but this is much less than that fixed by symbiotic bacteria, namely, 100–200 pounds per acre annually. These amounts obtain only for a favorable environment and may be much less otherwise.

Symbiotic bacteria grow mostly on the roots of a class of plants known as *legumes*, and such plants are characterized by nodules on the roots, the nodules being caused by and containing most of the bacteria. The bacteria live on the plant, that is, they obtain their necessary carbohydrate from the plant; at the same time they absorb nitrogen from the air, and this fixed nitrogen is then consumed by the plant to form proteins eventually. Both the plant and the bacteria are necessary in this cooperative process. Important members of the class of plants which are capable of acting as hosts to the symbiotic bacteria are peas, clover, alfalfa, and soy and other beans. It is now common practice to rotate crops so that the nitrogen content of the soils will not become depleted; that is, a few years devoted to plantings of non-legumes (cotton, wheat, corn, tobacco) are followed by plantings of legumes. The importance of fixed nitrogen in the soil was first clearly realized after 1862. [See Curtis, *Fixed Nitrogen* (chapter by Allison).]

The mechanism of the absorption of nitrogen by living organisms is not definitely known; that is, it is not known whether the first step consists in the formation of reduced (ammonia) nitrogen compounds or of oxidized or nitrate nitrogen. Nitrates when absorbed by plants are converted principally into proteins and other derivatives of ammonia.

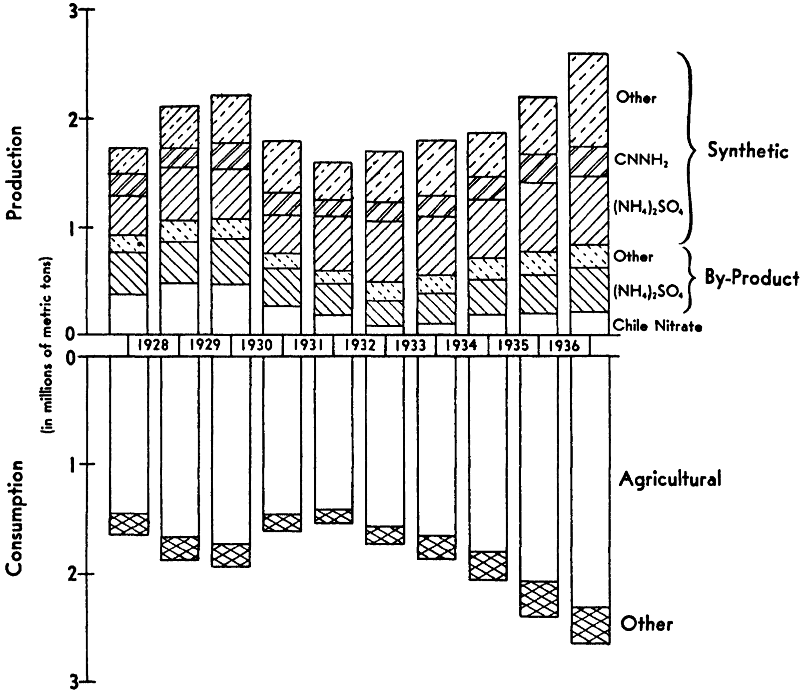


Fig. 14. World Production and Consumption of Nitrogen Compounds. The bars are for the "fertilizer years," 1927–1928, 1928–1929, etc. [Based on data from British Sulfate of Ammonia, Ltd.]

Nitrogen compounds are necessary for other than fertilizing purposes; thus dyestuffs, poisons, and explosives are usually nitrogen compounds or contain such compounds as an important constituent. In addition to such commodities, many others require for their manufacture the use of fixed nitrogen in one form or another; thus, the lead-chamber process for the manufacture of sulfuric acid and the conversion of cellulose to some types of fabrics require nitric oxide or acid. For this reason a great deal of attention has been given to methods for the conversion of atmospheric nitrogen to compounds of it. Before such methods became of economic importance, the principal sources of fixed nitrogen consisted of the by-product ammonium sulfate from the distillation of coal and mainly of the deposits of Chile saltpeter, $NaNO_3$, which, although found in many places, occur most abundantly in Chile. The Chile saltpeter was used directly or it was converted to nitric acid by the distillation of the salt with concentrate sulfuric acid. In 1913 Chile saltpeter provided about 55% of the world production of fixed nitrogen, but by 1929 this had decreased to 24%, although the number of tons of saltpeter mined was greater in 1929 than in 1913. The production of artificial fixed nitrogen rose from 7.3% of the total world production in 1913 to more than 50% in 1929. In 1913 the total world production of fixed nitrogen from all sources was 916,160 tons; in 1929 it was 2,324,300 tons. Still later, during the almost world-wide economic depression of 1931–1932, the total world production of fixed nitrogen was 1,553,704 metric tons, of which 170,000 metric tons was Chile nitrate [Read, *Industrial Chemistry*, John Wiley, N. Y., 1938]. As of January 1932 the total world capacity for production was 3,400,000 metric tons exclusive of Chile; the 1938 world production capacity was estimated to be five million tons. The 1933 production capacity was distributed as follows:

Country	Per Cent of World Production Capacity	Country	Per Cent of World Production Capacity
Germany	29	France	7.2
Chile	13 6	Japan	5.9
U. S. A	10.6	Others	26
Great Britain	7 7		

In 1935–1936 the world production was over 2,600,000 short tons, of which 8% was Chile nitrate, 17% from coal distillation, and 75% from synthetic ammonia processes. Changes in the sources of fixed nitrogen are shown in the following table in terms of percentages of world production. [For statistics to 1930, see Curtis, *Fixed Nitrogen.*]

	1900	1913	1934
Chile nitrate	66.6%	55.4%	6.9%
Coal	33.4	37.3	18.6
Air	0.0	7.3	74.5

The important processes for the artificial fixation of nitrogen depend on four different sets of reactions.

A. *The arc process.* In this process air is passed through an electric arc, and at the high temperatures obtaining there a small fraction, 1 to 2%, of the nitrogen is converted to NO. The yield is limited by the equilibrium state in the reaction $N_2 + O_2 = 2NO$ (see the section on NO, page 25). The emerging gases are rapidly cooled, and at ordinary temperatures the moderately slow reaction $NO + \frac{1}{2}O_2 = NO_2$ produces the dioxide, which is absorbed in water according to the important reversible reaction

$$3NO_2 + H_2O = 2HNO_3 + NO$$

The NO formed is oxidized to NO_2 by atmospheric oxygen, and the gas is then recirculated. The arc process, first perfected by Birkeland and Eyde, is no longer of importance; it has given way to the more convenient and economical synthetic ammonia and cyanamide processes. The cost of electric power and the problem of the oxidation and absorption of the dilute nitric oxide are the factors that militated against it.

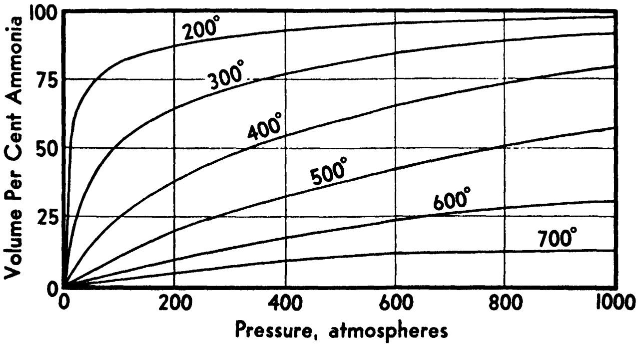


Fig. 15. The Equilibrium Percentage of Ammonia in the Reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$ as a Function of Pressure at Various Temperatures (in °C).

B. *The synthetic ammonia or Haber process.* A mixture of hydrogen and nitrogen under pressure and in the presence of an iron catalyst is caused to combine at 450–600° according to the reversible reaction

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$

The effect of temperature and pressure on the equilibrium constants of this reaction is shown graphically in Fig. 15 and in the following tables [Larson and Dodge, *J. Am. Chem. Soc.*, **45**, 2918 (1923); Larson, *ibid.*, **46**, 367 (1924)].

Table 16
VOLUME PERCENTAGE OF AMMONIA
IN 3:1 H_2-N_2 EQUILIBRIUM MIXTURES

Temp. (°C)	Pressure in Atmospheres						
	10	30	50	100	300	600	1000
300	14 73	30.25	39.41	52.04	70.96	84.21	92.55
400	3 85	10.15	15.27	25.12	47.00	65.20	79 82
500	1.21	3.49	5.56	10 61	26.44	42.15	57.47
600	0 49	1 39	2.26	4.52	13.77	23.10	31.43
700	0.23	0.68	1.05	2.18	7.28	12.60	12.87

Table 17
EMPIRICAL EQUILIBRIUM CONSTANTS FOR $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g)$

$$\text{Log}_{10} K_{P_{\text{atm}}} = \frac{\alpha}{T} + \beta \log_{10} T + \gamma T + \delta T^2 + I, \qquad K_{\text{atm}} = \frac{P_{NH_3}}{P_{N_2}^{\ 1/2} P_{H_2}^{\ 3/2}}$$

$$\alpha = 2074.8 \qquad \beta = -2.4943$$

Total Pressure (atm)	γ	$\delta \times 10^7$	I
10	0	1.856	1 993
30	-3.4×10^{-5}	1 856	2.021
50	-1.256×10^{-4}	1.856	2.090
100	-1.256×10^{-4}	1.856	2.113
300	-1.256×10^{-4}	1 8564	2.206
600	-1.0856×10^{-3}	1.8564	3.059
1000	$-2\ 6833 \times 10^{-3}$	1.8564	4.473

These equilibrium constants cannot be used directly for calculating free energies, since they refer to pressures and not fugacities. Although in the temperature range 300–700°C both nitrogen and hydrogen are nearly perfect gases even at high pressures, ammonia is far from being so; hence the *K*'s are to be regarded as empirical only, although they are extremely useful.[1]

---

[1] In order to write down thermodynamic equations, it is necessary to know not only the fugacities but also ΔH (22,000 cal) for $N_2(g) + 3H_2(g) = 2NH_3(g)$ and the heat capacities of the gases involved. The heat capacity of $NH_3(g)$ has been determined by Osborne, Stimson, Sligh, and Cragoe [*Sci. Papers, U.S. Bur. Standards*, 1924–1926, **65**] and is given in joules/g deg as a function of the pressure p (in meters of Hg) and temperature by the empirical formula

$$C_p = 1.1255 + 0.00238T + \frac{76.8}{T} + \frac{5.45 \times 10^8 p}{T^4} + \frac{(6.5 + 3.8p) \times 10^{27} p}{T^{12}} + \frac{2.37 \times 10^{42} p^6}{T^{20}}$$

The weight of one liter of ammonia gas at 760.00 mm and 0°C is 0.771409 grams [Moles and Roquero, *Añales Soc. españ. fis. quim.*, **35**, 263 (1937)].

The formation of ammonia is evidently favored by high pressures and low temperatures; but if the temperature falls to much below 400°C, the rate of the catalyzed reaction becomes too slow for the economical production of ammonia. If the temperature is too high, the equilibrium pressure of NH_3 is too low for satisfactory yields. Without a catalyst the reaction, which is heterogeneous, is much too slow to be of any use unless the temperature is quite high; and if the temperature is sufficiently high for a rapid rate (*ca.* 1000°), the equilibrium lies too far in favor of hydrogen and nitrogen to make the reaction of any practical value.

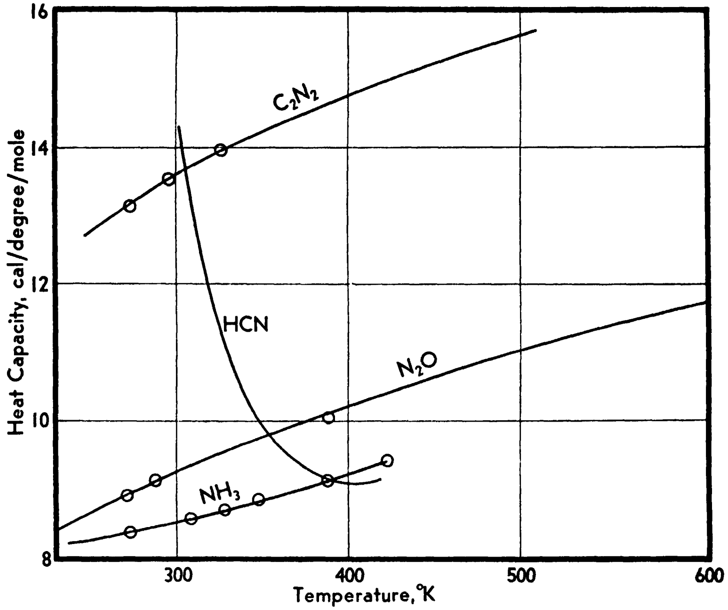


Fig. 16. The Molal Heat Capacity of Some Gaseous Nitrogen Compounds. N_2O: curve, calculated [Kassel, *J. Am. Chem. Soc.*, **56**, 1838 (1934)]; circles, experimental [Eucken and Lüde, *Z. physik. Chem.*, **5B**, 437 (1929)]. HCN: experimental [Felsing and Drake, *J. Am. Chem. Soc.*, **58**, 1714 (1936)]. NH_3: curve, calculated [Haupt and Teller, *J. Chem. Phys.*, **7**, 925 (1939)]; circles, experimental [Osborne, Stimson, Sligh, and Cragoe, *Sci. Papers U.S. Bur. Standards*, **1924/26**, 65]. C_2N_2: curve, calculated [Stevenson, *J. Chem. Phys.*, **7**, 171 (1939)]; circles, experimental [Bursik and Yost, *J. Chem. Phys.*, **7**, 1114 (1939)].

Many investigations have been made on the catalysts that are effective in ammonia synthesis, with the net result that finely divided iron containing small amounts of one or more "promoters" has been found to be most effective. The catalyst is usually prepared by reducing a heated mixture of Fe (1%), FeO, Fe_2O_3 (ratio of ferrous to ferric iron is about 0.57), Al_2O_3 (1.3%), and K_2O (0.2%), with a 3-to-1 mixture of hydrogen and nitrogen [see Curtis, *Fixed Nitrogen* (Emmett)]. Another procedure is to reduce a mixture of magnetite, Fe_3O_4, and the promoters Al_2O_3 and K_2O, or other oxides, with the hydrogen-nitrogen mixture.

The catalyst is rendered ineffective, "poisoned," by water, oxygen, and carbon monoxide and dioxide, and these substances must be removed from the hydrogen-nitrogen mixture which is to be converted to ammonia. In practice a purified hydrogen-nitrogen mixture is passed, under pressure and at a higher-than-ordinary temperature, first over a rugged catalyst that brings about the formation of a small amount of ammonia. The formation and removal of this ammonia facilitates the removal of any remaining "catalyst-poisons"—carbon compounds, if coke-oven gases are used as a source of hydrogen. The purified hydrogen-nitrogen mixture is then passed through strong-walled, steel cells containing the final catalyst. The temperature in the cells is maintained at about 450–500°; the heat of the reaction more than suffices for maintaining this temperature if high pressures are used and, indeed, makes it necessary to remove heat by proper cooling devices. The ammonia present in the gases emerging from the converters is caused to liquefy in tanks, from which it is periodically drawn off.

A complete mechanism of the catalyzed ammonia synthesis reaction has not been definitely established, but some significant hypotheses have been offered that may point the way to the eventual solution of the problem. The first step in the reaction is assumed to be the formation of an iron nitride by the reaction of nitrogen with very active surface atoms of iron. (Fe_4N and other iron nitrides are not stable at 450°, the equilibrium pressure of nitrogen above a Fe_4N—Fe mixture amounting to about 5000 atmospheres.) Hydrogen, too appears to be activated by the catalyst, since a very rapid conversion of para- to orthohydrogen is known to be effected by the catalysts used. Accordingly, the second concurrent step in the reaction may be supposed to consist of the activation of the hydrogen—no specific statement regarding the nature of this activation being at present possible, although the formation of monatomic hydrogen on the surface of the catalyst is not to be overlooked as a possibility. Finally, the activated hydrogen and Fe_4N may be supposed to react rapidly to form an intermediate NH, and this in turn to combine with further hydrogen to form NH_3.

The ammonia formed in the synthesis is either used as such, combined with acids to form ammonium sulfate or phosphate, or oxidized to nitric oxide with oxygen on a hot platinum gauze. In this oxidation process a mixture of ammonia (10%) and air is passed through a heated (750–900°) 80-mesh platinum gauze, where the reaction $4NH_3 + 5O_2 = 4NO + 6H_2O$ takes place to the exclusion of all but an inappreciable amount of the side reaction $4NH_3 + 3O_2 = 2N_2 + 6H_2O$. The nitric oxide is then further oxidized at ordinary temperatures to NO_2, and this is finally absorbed in water to form nitric acid.

C. *The cyanamide process.* This process involves the following independent reactions. Starting with naturally occurring limestone, $CaCO_3$, lime is formed:

$$CaCO_3(s) = CaO(s) + CO_2(g) \text{ at } 1100°$$

Then in an electric-arc furnace, the lime and carbon are caused to combine:

$$CaO(s) + 3C \text{ (coke)} = CaC_2(s) + CO(g), \qquad \Delta H = 121{,}150 \text{ cal}$$

The calcium carbide formed is then ground to such a fineness that it will pass through a 200-mesh screen. A few per cent, 2% or more, of powdered calcium fluoride, CaF_2, is mixed with the carbide and the mixture placed in a furnace. At 900° to 1000° the calcium carbide-calcium fluoride mixture absorbs nitrogen to form calcium cyanamide, $CaCN_2$.

$$CaC_2(s) + N_2 = CaCN_2(s) + C(s), \qquad \Delta H = -72{,}700 \text{ cal}$$

The nitrogen must be 99.8% pure or purer and is obtained by the fractional distillation of liquid air. In its applications the cyanamide is either used directly as a fertilizer or is hydrolyzed to produce ammonia. In either event it is desirable to spray it with a small amount of water to bring about the decomposition of any unreacted calcium carbide into $Ca(OH)_2$ and acetylene, C_2H_2. The hydrolysis is effected by autoclaving the cyanamide at somewhat above 100° with 3% sodium hydroxide solution:

$$CaCN_2 + 3H_2O = 2NH_3 + CaCO_3$$

Attention has been given to the mechanism of the nitrification reaction, with the result that the following steps are rendered probable [Polzenius, *Chem.-Ztg.*, **31**, 958 (1907); Krase and Yee, *J. Am. Chem. Soc.*, **46**, 1362 (1924); see also Krase in Curtis, *Fixed Nitrogen*]:

$$\begin{aligned} 3CaC_2 &= 3Ca + 6C \\ 3Ca + N_2 &= Ca_3N_2 \\ Ca_3N_2 + 3C + 2N_2 &= 3CaCN_2 \end{aligned}$$

D. *The alkali cyanide process.* This process, while very attractive in principle, has not proved as successful in practice as the cyanamide or synthetic ammonia process. The main reaction involved is the reversible one

$$Na_2CO_3 + 4C + N_2 + \text{Fe (catalyst)} \rightleftharpoons 2NaCN + 3CO + \text{Fe (catalyst)} \qquad \Delta H = 138{,}500 \text{ cal}$$

and it takes place at about 1000° to such an extent that cyanide yields of nearly 100% in laboratory experiments and 50% in practice are obtainable. The sodium cyanide is hydrolyzed at 400° to 500° with water, $NaCN + 2H_2O = NaHCO_2 + NH_3$, or it is treated with carbon dioxide to liberate HCN.

The fact that the main nitrifying reaction mixture is molten at 1000° and is a poor conductor of heat makes it difficult to bring it to the proper temperature. Moreover, good contact between the melt and nitrogen is difficult to attain, and satisfactory vessels resistant to the melt have not been found. The hydrolysis of the cyanide to ammonia also is accompanied by many practical difficulties. It is evident that more than one important factor is responsible for the lack of complete success of this process.

Nitric acid, HNO_3

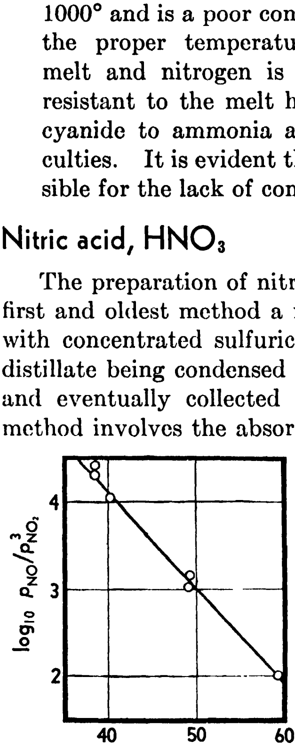


Fig. 17. The Equilibrium Concentration of HNO_3 in the Reaction $3NO_2 + H_2O = 2HNO_3 + NO$. Pressures are expressed in atmospheres.

The preparation of nitric acid is accomplished in two ways. In the first and oldest method a nitrate, Chile saltpeter for example, is mixed with concentrated sulfuric acid in a cast-iron retort and distilled, the distillate being condensed in a fused silica condenser cooled with water and eventually collected in stoneware or glass bottles. The second method involves the absorption in water of the NO_2 obtained from the arc process or from the oxidation of ammonia. The absorption reaction is reversible and is

$$3NO_2(g) + H_2O(l) = 2HNO_3(aq) + NO(g)$$

The equilibrium states in this reaction have been extensively investigated by both dynamic and static methods. [See Burdick and Freed, *J. Am. Chem. Soc.*, **43,** 518 (1921) (dynamic method); Abel, Schmid, and Stein, *Z. Electrochem.*, **36,** 692 (1930), and Chambers and Sherwood, *J. Am. Chem. Soc.*, **59,** 316 (1937) (static method).] It is evident that for a fixed concentration of nitric acid

$$\frac{P_{NO}}{P^3_{NO_2}} = K_1$$

and the value of K_1 will vary with the concentration of nitric acid. In Fig. 17 is reproduced Chambers and Sherwood's graphical representation of the results of all investigators for a range of acid concentrations. The complete equilibrium expression, in terms of partial pressures of $NO_2(g)$, $H_2O(g)$, $HNO_3(g)$, and $NO(g)$, is

$$\frac{P_{NO}P^2_{HNO_3}}{P^3_{NO_2}P_{H_2O}} = K$$

It is seen that the equilibrium constant depends upon the partial pressures of nitric acid and water as well as upon the ratio $P_{NO}/P^3_{NO_2}$. These partial pressures have been measured a number of times, but Forsythe and Giauque have recently pointed out [*J. Am. Chem. Soc.*, **64,** 48 (1942)] that the data do not obey the Duhem equation,

$$d \log_e P_{HNO_3} = -\frac{N_{H_2O}}{N_{HNO_3}} d \log_e P_{H_2O}$$

and are in fact unreliable by factors ranging to 2 or 3. The constants based on the experimentally determined partial pressures are correspondingly in error. However, by utilizing the experimental value of the entropy of nitric acid gas which they obtained and known thermodynamic properties of the other reactants, they were able to calculate the equilibrium constant as a function of temperature with the results shown in the following table.

TABLE 18
EQUILIBRIUM CONSTANTS FOR THE REACTION
$3NO_2(g) + H_2O(g) = 2HNO_3(g) + NO(g)$
$(\Delta H^\circ_0 = -7230 \text{ cal})$

T(°K)	K_{atm}	T(°K)	K_{atm}
275	3.78×10^{-2}	350	1.01×10^{-3}
293.1	1.37×10^{-2}	400	1.87×10^{-4}
298.1	1.05×10^{-2}	450	$4\ 86 \times 10^{-5}$
300	9.51×10^{-3}	500	1.65×10^{-5}

At 25°, $P_{NO}/P^3_{NO_2} = K_{1\,atm}$ varies from 2.75×10^4 for 37.1% HNO_3 to 1.00×10^2 for 58.8% HNO_3, and for still more concentrated acid $K_{1\,atm}$ is so small that the pressure of nitric oxide, for a moderate pressure of $NO_2(N_2O_4)$, becomes too small to permit of high concentrations of nitric acid being readily obtained by the absorption of NO_2 in water. This difficulty is partly overcome by passing a mixture of oxygen and nitrogen dioxide into water, the oxygen serving to oxidize the NO formed to NO_2, but the oxidation is slow and no catalyst for the reaction has been found. By employing a mixture of nitrogen dioxide and oxygen under pressure, much higher concentrations of nitric acid are obtainable, and this device is resorted to in practice to some extent. The rate of absorption of NO_2—N_2O_4 by water is rapid at first and then becomes slow as the concentration of HNO_3 increases—so slow, indeed, that for acid of greater than 50% strength the use of oxygen is required. Mixtures of liquid N_2O_4, water, and oxygen under pressures of 300 to 1000 pounds are sometimes used to obtain very strong (nearly 100%) nitric acid. Instead of resorting to high oxygen pressures to obtain the very concentrated nitric acid, it is more common to distill the weaker (50% or less) acid with concentrated sulfuric acid. The distillation of nitric acid alone does not lead to high concentrations, since 68.4% acid forms a constant boiling mixture boiling at 121.9°. Both reaction rates and equilibria are very important in the preparation or manufacture of nitric acid.

So far attention has not been concentrated on another reaction that takes place when NO_2 dissolves in water; namely,

$$2NO_2 + H_2O = H^+ + NO_3^- + HNO_2$$

This reaction is of importance when the concentration of nitric acid is very low, but at higher concentrations the reaction

$$3HNO_2 = H^+ + NO_3^- + H_2O + 2NO$$

goes practically to completion. In 20% nitric acid no detectable amount of nitrous acid is formed when NO_2 is absorbed. (See the section on nitrous acid for equilibrium constants and mechanism of this reaction.)

Table 19
VAPOR PRESSURES OF 100 PER CENT HNO_3

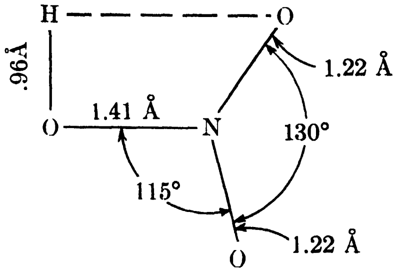
Temperature (°C)	Vapor Pressures (mm)	
	Taylor	Klemenc and Rupp
0		15.0
10	22	
12.5		30.8
20	42	
25	57	61.8
35	102	
50	215	
80	625	
85	720	
90	820	

Properties of nitric acid

Pure 100% nitric acid is a colorless liquid which boils at 83° and on cooling forms colorless crystals melting at −41.59°. At 25° the density relative to water at 4° is $D_4^{25} = 1.50269$. The vapor pressures of the 100% acid are appreciable even at room temperatures, as the accompanying table shows [Taylor, *Ind. Eng. Chem.*, **17**, 633 (1925)]. The experimental error in these measurements may be considerable. Some later values by Klemenc and Rupp [*Z. anorg. Chem.*, **194**, 51 (1930)] are given for comparison.

The 100% acid decomposes slowly into NO_2, O_2, and H_2O on exposure to light and on heating, with the result that it becomes colored. The equilibrium constants for the reaction are given in Table 20 [Forsythe and Giauque, *J. Am. Chem. Soc.*, **64**, 48 (1942)]. The pure acid is not as reactive in many reactions as its solutions; however, some substances are readily or explosively oxidized if warmed or heated with the 100% acid.

Spectroscopic studies indicate that the three oxygen atoms in HNO_3 lie at the corners of an equilateral triangle and are coplanar with the central nitrogen atom. Electron-diffraction experiments support this structure and give the accompanying distances and angles [Maxwell and Mosely, *J. Chem. Phys.*, **8**, 738 (1940). The O—H distance is assumed to be the same as in the water molecule].



The hydrogen atom is attached to one of the oxygen atoms with an H—O—N angle of roughly 90°. The possibility of forming a hydrogen bond (indicated by the dashed line) would be expected to cause a minimum at the NO_3 plane in the potential curve for rotation of the hydrogen about the (OH)—N bond. By comparing the entropy calculated from molecular constants with the experimental entropy, Forsythe and Giauque have found a double potential barrier of about 7000 cal/mole. The rotation of the hydrogen atom is thus greatly restricted and its motion at room temperature approximates closely a vibration of frequency 430 cm^{-1}.

TABLE 20
EQUILIBRIUM CONSTANTS FOR THE REACTION: $H_2O(g) + \frac{1}{2}O_2(g) + 2NO_2(g) = 2HNO_3(g)$
($\Delta H_0^{\circ} = -20{,}025$ cal)

T(°K)	K_{atm}
275	3.56×10^{5}
298.1	1.45×10^{4}
300	1.13×10^{4}
350	4.65×10
400	$4.43 \times 10^{-}$
450	2.81×10^{-2}
500	2.06×10^{-3}

Nitric acid and the solutions of nitric acid in water have been investigated repeatedly; the following tables and Fig. 18 present some of the more important physical properties. Two definite hydrates are known, the monohydrate, $HNO_3 \cdot H_2O$, which forms small, colorless opaque crystals with m.p. = −37.68°, and the trihydrate, $HNO_3 \cdot 3H_2O$, which exists as large, transparent crystals of m.p. = −18.47°.

Forsythe and Giauque (*loc. cit.*) have recently published the results of a thorough calorimetric study of nitric acid and its hydrates. The melting points, heat capacities, heats of fusion, and heats of dilution were directly measured. From the integral

$$\int_0^T \frac{C_p}{T}\,dT$$

the entropies were evaluated. For these entropies to be useful in thermodynamic calculations, it is necessary to know whether the experimental value represents all of the entropy, that is, whether any randomness in structure remained at the lowest temperatures reached (13°K). It is known, for instance, that in water there is a residual entropy after the customary extrapolation to 0°K of about $R \log_e \frac{3}{2} = .81$ cal/deg/mole due to a random orientation of hydrogen bonds (see the section on water), and it was possible that a similar phenomenon might be found in nitric acid. To rule out this possibility, it is necessary to find some reaction for which the ΔS from the calorimetric entropies based on the third law of thermodynamics can be compared with the ΔS derived from other independent measurements. Such a reaction is:

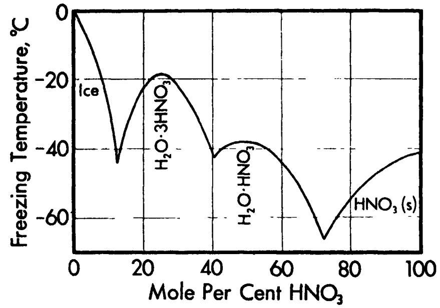


Fig. 18. Phase Diagram for the System H_2O—HNO_3. [Küster and Kremann, *Z. anorg. Chem.*, **41**, 1 (1904).]

$$HNO_3\ (l) + H_2O\ (l) = HNO_3{\cdot}H_2O\ (l)$$

or

$$HNO_3\ (l) + 3H_2O\ (l) = HNO_3{\cdot}3H_2O\ (l)$$

The free energy of hydration can be evaluated by means of the equation

$$\Delta F = RT \log_e \frac{P_{HNO_3}}{P^0_{HNO_3}} + 3RT \log_e \frac{P_{H_2O}}{P^0_{H_2O}} \quad .$$

where the P^0's refer to the vapor pressures of the pure components, and the P's refer to the partial pressure of the components over the solution. From the heat-of-solution measurements, the heat of reaction, ΔH, can be calculated. The entropy change is then given by

$$\Delta S = \frac{\Delta H}{T} - \frac{\Delta F}{T}$$

Agreement of this value of ΔS with the ΔS obtained from the third law of thermodynamics would prove that if there is residual entropy, it is the same for the pure acid and its hydrates. As the structures are necessarily different, the residual entropy would most probably be zero.

In attempting to carry out this comparison, Forsythe and Giauque found, as has been previously mentioned, that much of the available

TABLE 21
PHYSICAL PROPERTIES OF NITRIC ACID SOLUTIONS

Density (Relative) of HNO_3 Solutions at 20°

Weight Per Cent HNO_3	D_4^{20}	Weight Per Cent HNO_3	D_4^{20}	Weight Per Cent HNO_3	D_4^{20}
1	1.00364	40	1.2463	80	1.4521
10	1.0543	50	1.3100	90	1.4826
20	1.1150	60	1.3667	95	1.4932
30	1.1800	70	1.4134		

Partial Vapor Pressures in mm, $p_{H_2O}(=p_W)$ and $p_{HNO_3}(=p_A)$, of HNO_3 Solutions
[See Taylor, *Ind. Eng. Chem.*, **17**, 633 (1924), for results of several investigators.]

Weight Per Cent HNO_3	t(°C)							
	10		25		50		100	
	p_W	p_A	p_W	p_A	p_W	p_A	p_W	p_A
20	8.0	—	20.6	—	80	—	675	1.87
30	7.1	—	17.8	—	69	0.25	580	6.05
50	4.2	0.12	10.7	0.39	42.5	2.18	383	34.2
60	3.0	0.41	7.7	1.21	31.0	5.68	285	69.5
80	1.2	4	3.2	10.5	12	41	108	330
90	—	11	1	27	4	103	35	675
100	—	22	—	57	—	215	—	>900

Examination of Partial Pressure Data for HNO_3 Solutions by the Duhem Equation and with the Aid of the Calorimetric Entropies
[Forsythe and Giauque, *J. Am. Chem. Soc.*, **64**, 48 (1942); data of Wilson and Miles, *Trans. Faraday Soc.*, **36**, 356 (1940).]
(All pressures are for 20°C.)

Weight Per Cent HNO_3	p_{H_2O}		p_{HNO_3}	
	Obs. (mm)	From Curve	Obs. (mm)	From Curve
49.94	7.75	7.9	0.355	0.183
53.83 ($HNO_3 \cdot 3H_2O$)	—	(6.77)	—	(0.345)
69.70	2.92	2.62	2.88	2.90
77.77 ($HNO_3 \cdot H_2O$)	—	(1.10)	—	(8.43)
86.72	0.50	0.201	25.70	25.84
91.2	0.35	0.146	29.11	29.07
96.48	0.11	0.028	41.59	41.59

TABLE 21 (*Cont.*)

Activity Coefficients, γ, of Nitric Acid at 25°

[Hartman and Rosenfeld, *Z. Phys. Chem.*, **164A**, 385 (1933); Redlich, *Landolt-Bornstein-Roth*, Erg. Bd. 2, p. 1119.]

(Concentrations, m, in moles per 1000 g water. $\gamma = a^{1/2}/m$.)

m	γ	m	γ	m	γ
.001	0.9660	1.0	7235		
.005	9295	2	.7931	16	1.45
.01	.9053	3	.9090	20	2.2
.05	.8280	4	1.1	36	2.18
0.1	.7909	9	1.16	50	2.5
.5	.7197	10	1.45	100	2.1

Heat of Dilution of HNO_3 at Room Temperature

H refers to 1 mole HNO_3 with n moles H_2O

h refers to 1 mole H_2O with N moles HNO_3

$$H = \frac{8974n}{n + 1.737} \text{ cal}, \qquad h = \frac{8974N}{1 + 1.737N} \text{ cal}$$

data on the partial pressures of nitric acid and water over nitric acid solutions are not self-consistent when tested by the Duhem equation. However, they were able to find two sets of data which were in agreement with the Duhem equation. The test for residual entropy gave the following results:

$$\begin{aligned} HNO_3\text{ (l)} + H_2O\text{ (l)} &= HNO_3{\cdot}H_2O \\ \Delta S_{343.1} &= -2.13 \text{ cal/deg} && \text{(third law)} \\ &= -2.21 && \text{(from } \Delta F \text{ and } \Delta H \text{ values)} \\ HNO_3\text{ (l)} + 3H_2O\text{ (l)} &= HNO_3{\cdot}3H_2O \\ \Delta S_{323.1} &= 4.65 \text{ cal/deg} && \text{(third law)} \\ &= 4.64 && \text{(from } \Delta F \text{ and } \Delta H \text{ values)} \end{aligned}$$

The excellent agreement indicates that nitric acid and its mono- and trihydrate approach zero entropy as they approach the absolute zero of temperature. The calorimetric entropies are thus the appropriate ones to use in thermodynamic calculations.

In addition to the ordinary concentrated and dilute nitric acid solutions that are commonly met with in the laboratory and in industrial plants, there is also the red, fuming nitric acid that can be purchased in the market. Red, fuming nitric acid consists of concentrated nitric acid in which is dissolved variable amounts of NO_2; the specific gravity of the commercial product is about 1.59 to 1.60. The acid is sometimes made by adding a small amount of organic reducing agent, for example, formic acid, to the ordinary concentrated acid, the NO_2 produced being absorbed in the nitric acid itself. The solvent action of the red, fuming acid is much more rapid than that of ordinary concentrated nitric acid owing to the presence of the NO_2. The role played by the nitrogen dioxide is not completely understood notwithstanding the great amount of discussion concerning it.

TABLE 22
THE THERMODYNAMIC PROPERTIES OF NITRIC ACID AND ITS HYDRATES
[Forsythe and Giauque, *J. Am. Chem. Soc.*, **64,** 48 (1942); heat of vaporization, Wilson and Miles, *Trans. Faraday Soc.*, **36,** 356 (1940).]
(0°C = 273.1°K)

	HNO_3	$HNO_3 \cdot H_2O$	$HNO_3 \cdot 3H_2O$
Melting point (°K)......	231.51	235.48	254.63
Heat of fusion (cal/mole)... ...	2503	4184	6954
Heat of vaporization at 293.1° (cal/mole)................ ..	9426		
Heat capacity, (cal/deg mole):			
220°..	15.82(s)	19.81(s)	35.51(s)
240.....	26.70(l)	43.02(l)	38.67
260......... .	26.59	43.32	74.99(l)
280......	26.42	43.48	76.72
300..........	26.24	43.62	77.80
ΔH of infinite dilution at 298.1° (cal/mole)................ .. .	−7971	−4732	−2132
Entropy of liquid at 298.1° (cal/deg/mole)................ .	37.19	51.84	82.93
Entropy of gas at 298.1° (cal/deg/mole)........	63.62		

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}O_2 + \tfrac{1}{2}H_2 = HNO_3(l)$$
$$\Delta H_{298.1} = -41{,}349 \text{ cal}, \qquad \Delta F^{\circ}_{298.1} = -19{,}030 \text{ cal}$$
$$\tfrac{1}{2}N_2 + \tfrac{3}{2}O_2 + \tfrac{1}{2}H_2 = HNO_3(g)$$
$$\Delta H_{298.1} = -31{,}994 \text{ cal}, \qquad \Delta F^{\circ}_{298.1} = -17{,}948 \text{ cal}$$
$$\tfrac{1}{2}N_2 + \tfrac{3}{2}O_2 + \tfrac{1}{2}H_2 = HNO_3(\text{aq. } a = 1)$$
$$\Delta H_{298.1} = -49{,}320 \text{ cal}, \qquad \Delta F^{\circ}_{298.1} = -26{,}345 \text{ cal}$$

(Note: There was an arithmetical error in the ΔF°'s in the original paper The above values are correct.)

Nitric acid is an oxidizing agent, and it is this property that makes the substance especially useful and valuable. In its reactions the reduction products are variable; thus, at low concentrations the reduction product is principally NO, while the concentrated acid yields considerable NO_2. The reactions may be typified as follows, where R is a reducing agent:

$$2H^+ + 2NO_3^- + 3R = 3RO + 2NO + H_2O \qquad \text{(Dilute acid)}$$
$$2H^+ + 2NO_3^- + R = RO + 2NO_2 + H_2O \qquad \text{(Concentrated acid)}$$

It must not be supposed, however, that the reactions in any given mixture may be represented simply by one or the other of these equations. Both

NO and NO_2 will be found as reduction products with one of the oxides usually predominating.

When nitric acid is added to such metals as pure copper, lead, silver, and others, the oxidation is often slow at first; but once started, for example, by warming, the reaction continues vigorously until the metal is dissolved or the concentration of acid becomes low. Without warming, the reaction may be initiated by dissolving a small amount of NO_2 in the mixture. This noteworthy fact has suggested to many chemists that the mechanism of the oxidation of metals involves nitrous acid. Thus considering the rapid reversible formation of N_2O_4 from NO_2, the mechanism would be expressed by the reactions

$$\begin{aligned} N_2O_4 + H_2O &= H^+ + NO_3^- + HNO_2 \\ Cu + 2HNO_2 &= Cu^{++} + 2NO + H_2O \\ 4H^+ + 4NO_3^- + 2NO &= 3N_2O_4 + 2H_2O \end{aligned}$$

the extent of the last reaction depending on the concentration of nitric acid. If the acid is dilute, equilibrium in the last reaction lies to the left, and if concentrated to the right. Oxidation by dilute acid would, therefore, yield mainly NO, and with concentrated acid the product would be NO_2. Such a simple mechanism would probably not suffice to explain the oxidizing action in all its details; to do this the actual or possible formation of ammonia, hydroxylamine, hyponitrous acid, and other lower-valence compounds of nitrogen are invoked. The evidence for some of the detailed mechanisms offered is not altogether sufficient or satisfying. It would add a great deal to the subject if a very thorough investigation of the rate of some reaction involving nitric acid as an oxidizing agent were made; thus the oxidation of Sn^{++}, Ti^{++}, I^-, Br^-, or some other reducing agent could probably be studied and the mechanism determined in some range of concentrations for which the rate would be measurable. The reader is referred to the literature for a detailed discussion of the notions held by some investigators of the mechanisms of nitric acid oxidation reactions. [See Veley, *Proc. Roy. Soc.*, **52,** 27 (1893); Veley and Manley, *Phil. Trans.*, **191 A,** 365 (1898); *ibid.*, **182 A,** 312 (1891); Acworth and Armstrong, *J. Chem. Soc.*, **32,** 56 (1877); Banerji and Dhar, *Z. anorg. Chem.*, **122,** 73 (1922); Bancroft, *J. Phys. Chem.*, **28,** 475, 973 (1924).] It may be added that the theory of nascent hydrogen, that is, freshly formed hydrogen (possibly monatomic hydrogen or an activated hydrogen molecule), in this connection is not regarded with as much favor as formerly, owing to the fact that its presence during reaction has not been susceptible to satisfying proof.

Dilute nitric acid is usually slow in its action; thus, in a solution of a strength of a few tenths normal, iodine is liberated but slowly from iodides, and bromine scarcely at all from bromides. At high concentrations iodine, bromine, and even chlorine are liberated rapidly from halide salts. Iodine is oxidized slowly to iodate by strong nitric acid. Mixtures of strong nitric and hydrochloric acids have long been known as *aqua regia* and are so called because of their solvent action on the noble metals, principally gold, platinum, and other elements of the platinum group. From a thermodynamic point of view, concentrated nitric acid alone is capable of oxidizing gold in the presence of substances forming gold complexes. But the presence of the nitrosyl chloride, resulting from the interaction of the concentrated nitric and hydrochloric acids, appears to catalyze the reactions greatly, whereas nitric acid alone acts only very slowly.

Mixtures of concentrated nitric and sulfuric acid have found considerable application in organic chemistry as reagents for adding or substituting a nitro group, —NO_2, in an organic compound.

Nitric acid is a strong acid, and salts of it with strong bases are, in aqueous solution, neutral to litmus. The nitrates in general are characterized by being soluble in water. A few organic nitrates, for example, nitron nitrate, 1,5-diphenylanilodihydrotriazol nitrate, are very slightly soluble and may be used for the gravimetric determination of nitrates. The following table presents the solubilities of some typical neutral or nearly neutral inorganic nitrates [Int. Crit. Tables].

TABLE 23

SOLUBILITIES OF SOME NITRATES IN WATER

(The solubilities are expressed in formula weights per 1000 g of water.)

Temp. (°C)	Li	Na	K	Rb	Cs	NH_4	Ca
0	7.3, $3H_2O$	8.62	1.30	1.33	0.47	15.48	6.22, $4H_2O$
25	12.4, $3H_2O$	10.80	3.74	5.55 (30°)	1.86 (30°)	29.75 (30°)	8.41, $4H_2O$
100	33.9	20.64	24.50	30.5	10.10	129.5	22.1
	Sr	Mg		Ba	Pb	Ag	Tl
0	1.89, $4H_2O$	4.48, $6H_2O$		0.190	1.217	6.65	0.149
25	3.75, $4H_2O$	5.00 (20°) $6H_2O$		0.445 (30°)	1.80	14.00	0.535 (30°)
100	4.80	9.95 (90°) $6H_2O$		1.32	3.79	57.8	15.3

The configuration of the nitrate ion, as determined by X-ray studies on crystals of $NaNO_3$, is that of an equilateral triangle, the three oxygen atoms occupying the corners and the nitrogen atom the center. The oxygen atoms and the nitrogen atom all lie in the same plane. The N—O distance is 1.21 Å, a distance which indicates that the bonds have a mixture of single- and double-bond character, and that in addition there is a formal positive charge on the nitrogen and negative charges on two of the oxygens; as a result of assumed resonance between the double and single bonds, all three N—O distances are equal. [See Elliott, *J. Am. Chem. Soc.*, **59**, 1380 (1937); Pauling, *The Nature of the Chemical Bond*, 2nd Ed., Cornell University Press, 1940.] If all bonds were single, the N—O distance would be 1.36 Å; if double, 1.18 Å.

The commonly applied test for nitrates, namely, that of carefully pouring concentrated sulfuric acid down the inside of a test tube containing a solution of the nitrate and $FeSO_4$ so that two layers are formed, depends on the formation of the dark-colored complex $FeNOSO_4$ which appears as a "ring" at the top of the acid layer. Ferrous iron in strong acid serves also to reduce the nitrate to NO; nitrites behave in the same manner in this test. Diphenylamine or diphenylamine sulfonic acid in sulfuric acid solution are colored blue by nitrates [Tillmanns, and Sutthoff, *Z. anal. Chem.*, **50**, 485 (1911); Kolthoff and Noponen, *J. Am. Chem. Soc.*, **55**, 1448 (1933)]. A reagent commonly used for the colorimetric estimation is phenoldisulfonic acid, which gives a yellow color with even very small amounts of nitrate [Chamot, Pratt, and Redfield, *J. Am. Chem. Soc.*, **33**, 366, 382 (1911); Arny and Ring, *Ind. Eng. Chem.*, **8**, 309 (1916)]. For larger quantities of nitrate, the quantitative determination can be accomplished by the reduction in neutral, acid, or alkaline solution to ammonia. The reducing agent used is ordinarily an alloy, for example, Dvarda's alloy (45% Al, 50% Cu, and 5% Zn), and the ammonia formed on the addition of NaOH is distilled into an excess of standard acid solution, the excess being determined with a standard base.

Of importance in analysis is the reaction between hot concentrated nitric acid and ammonium salts in the presence of hydrochloric acid. The ammonium radical is oxidized completely to nitrogen and oxides of nitrogen; the reaction thus serves for the destruction of ammonium salts and accomplishes it in a much more convenient manner than does the volatilization process often used [Swift, *A System of Chemical Analysis*, Prentice-Hall, N. Y., 1939, p. 362]. Hydrogen sulfide reacts but slowly if at all with nitric acid solutions containing less than 5% HNO_3. More concentrated solutions react with H_2S to form S, NO_2, NO, N_2, and a small amount of ammonium salts. Titanous salts, Ti^{+++}, reduce nitric acid solutions principally to NO, some N_2O, and N_2 with traces of NO_2 and NH_2OH [Milligan and Gillette, *J. Phys. Chem.*, **28**, 747 (1924)]. When Fe^{++} is warmed with acid nitrate solutions, the reduction of nitrate ion to NO is quantitative. In alkaline solutions (20% NaOH) nitrate is reduced quantitatively to ammonia. The reaction between sulfur dioxide and nitric acid is an important one in the lead-chamber process for the manufacture of sulfuric acid. With

1:100 HNO_3 solutions, a slow reaction yielding N_2O and H_2SO_4 takes place; with stronger acid, NO_2 and blue solutions (HNO_2) result; with acid of specific gravity 1.16 to 1.22, NO_2 and green solutions result; but if concentrated nitric acid of specific gravity 1.50 or greater is treated with SO_2, there is formed the so-called lead-chamber crystals or nitrosyl bisulfate, $NOHSO_4$. The colorless crystals are obtained readily if SO_2 is bubbled through chilled (0°C) fuming nitric acid.

CHAPTER 3

Hydroxylamine, Amine Sulfonates, Phosphorus Chloronitrides, Hydrazine, and Hydrazoic Acid

Hydroxylamine and Hydroxylamine Sulfonates

The interesting chemistry of hydroxylamine and its derivatives has attracted the attention of chemists for many years. The names of Fremy (1845), Claus, Divers, Haga, and Raschig are to be associated with this field of nitrogen chemistry; it was by them that much of the original work was done. In the following list are presented the formulas and names of the more important inorganic derivatives of hydroxylamine. The majority of them are stable only as their salts, and for these the negative ion is shown in brackets.

$HONH_2$	Hydroxylamine.
$[HONHSO_3]K$	Hydroxylamine monosulfonate.
$[HON(SO_3)_2]K_2$	Hydroxylamine disulfonate.
$[SO_3ON(SO_3)_2]K_3$	Hydroxylamine trisulfonate.
$[SO_3ONHSO_3]K_2$	Hydroxylamine isodisulfonate.
$[SO_3ONH_2]H$	Hydroxylamine isomonosulfonate.
$[ON(SO_3)_2]K_2$	Nitrosyl disulfonate.

Although hydroxylamine is formed in a variety of reactions [NO + Sn (in conc. HCl) + $PtCl_4$ (catalyst), $C_2H_5NO_2$ + Sn (in HCl)], two methods of preparation are outstanding. In the first and most important practical method, a sulfuric or hydrochloric acid solution containing HNO_3 or $NaNO_3$ is electrolyzed; 50% H_2SO_4 gives the best results, and the concentration of nitrate should be kept low to obtain the highest yields. The yield is strongly influenced by the electrode material; with amalgamated lead electrodes the highest yield, about 65%, is obtained. Other electrodes, for example, Cu and Pt, give rise to very low yields, but mercury alone when properly used is capable of leading to good yields [see, for example, Tafel, *Z. anorg. Chem.*, **31,** 289 (1902); Schtscherbakow and Libina, *Z. Electrochem.*, **35,** 826 (1929)]. After the electrolysis of the sulfuric acid solutions, the resulting mixture is neutralized, converted to the chlorides with $BaCl_2$, evaporated to dryness, and then extracted with alcohol in order to obtain the alcohol soluble hydroxylamine hydrochloride. Hydroxylammonium chloride (hydroxylamine hydrochloride), NH_2OH_2Cl, is a white crystalline salt which is quite stable at ordinary temperatures and can be kept indefinitely in glass bottles; on heating, the solid salt decomposes. It is soluble in water to the extent of 83 grams per 100 grams of water at 17°. The nitrate, NH_2OHHNO_3, is more soluble and the sulfate, $(NH_2OH)_2H_2SO_4$, less soluble than the chloride; when heated, the solid nitrate decomposes into nitric oxide, water, and other products.

In the second method of preparation, a nearly neutral alkali nitrite solution is treated with SO_2 or a bisulfite at 0° to −5°. It is essential for good yields that the concentration of H^+ does not exceed about 5×10^{-5} moles/l.

This condition is to some extent fulfilled if the $NaNO_2$ and Na_2CO_3 are dissolved together in water and the resulting solution treated with SO_2 (at 0° to −5°) until the odor of it is just detectable. A recent improved modification of the method is one in which advantage is taken of the buffer action of potassium acetate-acetic acid solutions. In this method [Rollefson and Oldershaw, *J. Am. Chem. Soc.*, **54,** 977 (1932)], 1 mole KNO_2 + 1.2 mole KCH_3CO_2 are dissolved in 200 cc of ice water. After adding 1500 g of finely divided ice, SO_2 is passed slowly into the mixture until the odor of it is just detectable. During the addition of SO_2, the solution remains colorless, and the moderately soluble salt $HON(SO_3)_2K_2$, potassium hydroxylamine disulfonate, crystallizes out. If the temperature rises above 0° during the reaction, the solution becomes yellow in color, and nitric oxide and amine trisulfonate (nitrilosulfonic acid), $H_3N(SO_3)_3$, become the products of the reaction; it is only at the lower temperatures that the rate of reduction of nitrite to hydroxylamine disulfonate is greater than the rate of formation of amine trisulfonate. The reaction is

$$NO_2^- + 2HSO_3^- + H^+ = HON(SO_3)_2^= + H_2O$$

Freshly prepared aqueous solutions of $HON(SO_3)_2K_2$ are neutral to litmus but are only moderately stable; when the solutions are made acid, they hydrolyze fairly rapidly to hydroxylamine monosulfonate ion, $HONHSO_3^-$. Because of its strong tendency to hydrolyze, nothing of an exact nature is known about the strength of the acid $[HON(SO_3)_2]H_2$; but since solutions of the alkali salts are neutral, the acid must be at least as strong as sulfuric acid. The rate of hydrolysis is proportional to the concentrations of $(SO_3)_2NOH^=$ and H^+, and the rate is measurable at 25° when the concentration of H^+ is in the neighborhood of 0.005 n or less [Wagner, *Z. phys. Chem.*, **19,** 668 (1896)]. Even initially neutral solutions of the disulfonate slowly become acid, owing to the hydrolysis. The hydrolytic reaction is

$$(SO_3)_2NOH^= + H_2O = (SO_3)HNOH^- + H^+ + SO_4^=$$

Some recent measurements by Naiditch and Yost [*J. Am. Chem. Soc.*, **63,** 2123 (1941)] show that the rate equation is

$$-\frac{d(\mathrm{HON(SO_3)_2^{=}})}{dt} = k(\mathrm{HON(SO_3)_2^{=}})(\mathrm{H^+})$$

k has the value 0.20 mole/l min at 25°, if the concentration of disulfonate is in the neighborhood of 0.1 m. The mechanism involves $[\mathrm{HON(SO_3)_2H}]^-$ as the reactive intermediate. In alkaline solution, the rate of hydrolysis is much slower. The solid dry salt $K_2(SO_2)_2NOH{\cdot}2H_2O$ can be kept for only a comparatively short time; after a day or so (or less, if moisture is present), the odor of SO_2 can be noted. The anhydrous salt may be prepared by washing the dihydrate with absolute alcohol; in the absence of moisture $K_2(SO_3)_2NOH$ does not decompose, and it differs from the dihydrate in this respect. The solubility of the dihydrate in water or very dilute alkali amounts to 23.0 g per liter of solution at 0°; that is, at 0° the saturated solution is 0.075 molar in the salt. The solutions are not strong oxidizing agents; they react with PbO_2, $KMnO_4$, and Ag_2O to form nitrosyl disulfonate (peroxylamine sulfonate) ion, $ON(SO_3)_2^{=}$, a substance which is discussed in detail below.

The potassium monosulfonate, $HONHSO_3K$, that results from the hydrolysis of the disulfonate, can be crystallized without difficulty from its solutions. The solutions are neutral to litmus, and hence the acid $[HONHSO_3]H$ is strong. When the salt or acid in 0.5 n HCl is heated at 100° for an hour or so, it hydrolyzes completely to form sulfate and hydroxylammonium ions.

$$\mathrm{SO_3HNOH^- + H_2O = H_2NOH{\cdot}H^+ + SO_4^{=}}$$

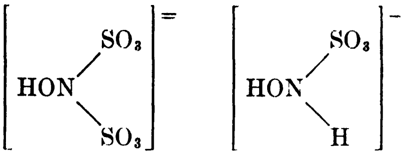
Owing to the weakly basic character of hydroxylammonium hydroxide, the solution becomes distinctly acid; the rate of hydrolysis has not been measured.

Solutions of hydroxylamine monosulfonate ion resemble, in their reducing action, those of hydroxylamine itself; thus, they may be titrated with iodine solutions, the reaction being

$$\mathrm{2SO_3HNOH^- + 2I_2 + H_2O = N_2O + 4H^+ + 4I^- + 2HSO_4^-}$$

When boiled with alkali, the monosulfonate decomposes to give sulfites, nitrous oxide, and, under some conditions, hyponitrites.

Hydroxylamine can be regarded as a derivative of ammonia, NH_3, in which one hydrogen is replaced by a hydroxyl group. On the basis of this picture, the disulfonate is a derivative of hydroxylamine in which the two hydrogens attached to the nitrogen atom are replaced by two sulfonate groups. Inasmuch as the salts are completely ionized in aqueous solution, we may write the disulfonate and monosulfonate ions as



The hydroxyl hydrogen in the disulfonates behaves as a very weakly acidic hydrogen and may be neutralized with concentrated KOH to give the salt $K_3[ON(SO_3)_2]$. This salt hydrolyzes rapidly and reversibly in water to give alkaline solutions, and the solutions decompose slowly into KNO_2 and K_2SO_3.

If a neutral or alkaline solution of $HON(SO_3)_2K_2$ is treated with PbO_2, $KMnO_4$, or Ag_2O at room temperature or even somewhat above, the solution slowly becomes violet-blue in color, and from it a yellow salt may be crystallized which has the empirical formula $ON(SO_3)_2K_2$. This yellow salt dissolves in water to give violet-blue solutions identical in appearance to those from which the yellow salt is crystallized; it was suggested earlier that the solution contains monomeric $ON(SO_3)_2^=$ and that the salt consists of the dimer $[ON(SO_3)_2]_2K_4$. This view has been confirmed by Asmussen [*Z. anorg. Chem.*, **212,** 317 (1933)], who found the solutions to be paramagnetic and the solid salt to be diamagnetic. The molal susceptibility found by Asmussen for the solutions corresponds to a single unpaired electron in an *S* state. The monomeric ion $(SO_3)_2NO^=$ contains an odd number of electrons, and, according to the Lewis-Sidgwick-Bose rule, it should be paramagnetic; the dimer would contain an even number of electrons and, if these electrons are all paired and are in *S* states, the compound would be diamagnetic. These facts indicate that $ON(SO_3)_2^=$ may be considered as a derivative of NO_2 in which an oxygen atom is replaced by two sulfonate groups.

The violet-blue solutions of $ON(SO_3)_2^=$ are only moderately stable; after one or two weeks in a solution of dilute KOH, the intensity of the color, which is considerable in 0.1 m solutions, decreases so that the solutions become practically colorless; in acid rapid decomposition takes place. The colored solutions are good oxidizing agents and will liberate iodine from iodides.

$$ON(SO_3)_2^= + I^- + H^+ = HON(SO_3)_2^= + \tfrac{1}{2}I_2$$

[Raschig, *Lieb. Ann.*, **241,** 161 (1887); Divers and Haga, *J. Chem. Soc.*, **77,** 440 (1900).] The salt $K_4[(SO_3)_2NO]_2$ is soluble in 0.1 n KOH to the extent of 6.6 grams per 100 grams of solvent at 29° and 0.62 grams at 0°, and the solutions of the salt in water are neutral before decomposition sets in. The solid salt decomposes with time into SO_2, N_2O, and ammonium sulfate.

The decomposition of the alkaline solutions of $ON(SO_3)_2^{=}$ leads to hydroxylamine trisulfonate, $SO_3ON(SO_3)_2^{\equiv}$, that is, a compound which may be regarded as a derivative of the disulfonate in which the hydroxyl hydrogen is replaced by a sulfonate group.

Hydroxylamine trisulfonate can be prepared by heating gently an alkaline solution of $K_2[HON(SO_3)_2]$ with lead dioxide for an hour or more. The mixture becomes at first violet-blue in color, but on continued warming the color fades completely. From the resulting cooled and filtered solution large, beautiful, colorless crystals of $K_3[(SO_3)_2NOSO_3]$ separate after a few hours. X-ray photographs show the crystal structure to be very complex. The reaction takes place in steps, as is evidenced by the fact that the solution becomes first violet-blue ($[(SO_3)_2NO]^{=}$) and then colorless. The two steps in the reaction may be written

$$\begin{aligned} 2(SO_3)_2NOH^{=} + PbO_2 &= 2(SO_3)_2NO^{=} + PbO + H_2O \\ 4(SO_3)_2NO^{=} + OH^{-} &= 2(SO_3)_3NO^{\equiv} + (SO_3)_2NOH^{=} + NO_2^{-} \end{aligned}$$

the net effect being

$$3(SO_3)_2NOH^{=} + 2PbO_2 + OH^{-} = 2(SO_3)_3NO^{\equiv} + NO_2^{-} + 2PbO + 2H_2O$$

This equation includes most but not all of the products formed in the reactions. Raschig describes a method of preparation that is more direct but does not differ in principle from that just outlined [Raschig, *Ber.*, **56**, 206 (1923)]. 1200 cc of cooled 5 n $NaHSO_3$ solution are added slowly to a previously stirred mixture of 100 g of $NaNO_2$ and 1000 g of ice. When the reaction is complete, 600 g of PbO_2 are slowly added with continual stirring. The resulting alkaline solution is treated with 800 g of KCl and placed in an icebox to crystallize. The yield is 800 g of $K_3[(SO_3)_2NOSO_3]\cdot 2H_2O$. The net reaction with the hydroxylamine disulfonate formed is said to be

$$K_2[(SO_3)_2NOH] + K_2SO_3 + PbO_2 = PbO + K_3[(SO_3)_2NOSO_3] + KOH$$

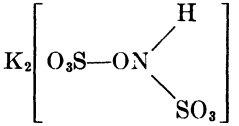
Still another reaction producing the trisulfonate is that between $KHSO_3$ and $[(SO_3)_2NO]^{=}$, equal molal quantities of tri- and disulfonate being formed.

The potassium hydroxylamine trisulfonate $K_3[(SO_3)_2NOSO_3]\cdot 2H_2O$ is soluble in water to the extent of 25.4 grams per 100 grams of solvent at 18°. One part of the sodium salt dissolves in 2.8 parts of water at 21.5°. The solutions are neutral to litmus, and when made alkaline are not affected by permanganate, lead dioxide, or KClO. When solutions of the trisulfonate are carefully acidified with HCl, so that the final concentration is 0.01 n or less, they hydrolyze rapidly to give hydroxylamine isodisulfonate [Raschig, *Ber.*, **39,** 245 (1906)].

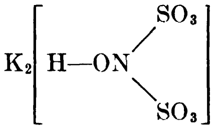
$$(SO_3)_2NOSO_3^{=} + H_2O = SO_3HNOSO_3^{-} + H^+ + SO_4^{=}$$

The rate of this reaction is measurable at room temperatures and in quite dilute acid (0.01 n or less) solutions. The few measurements made on the reaction by Wagner [*Z. phys. Chem.*, **19,** 668 (1896)] do not suffice to conclude more than that the rate appears to be directly proportional to the trisulfonate and hydrogen ion concentrations. When one drop of sulfuric or hydrochloric acid is added to a moderate volume of a $K_3(SO_3)_2NOSO_3$ solution, some three or four days are required for complete hydrolysis to the isodisulfonate.

The hydroxylamine isodisulfonate is an isomer of the normal disulfonate described above. One of the sulfonate groups in the isodisulfonate occupies the place occupied by the hydroxyl hydrogen in the normal disulfonate; that is, the two forms may be written as follows:



(Hydroxylamine isodisulfonate)



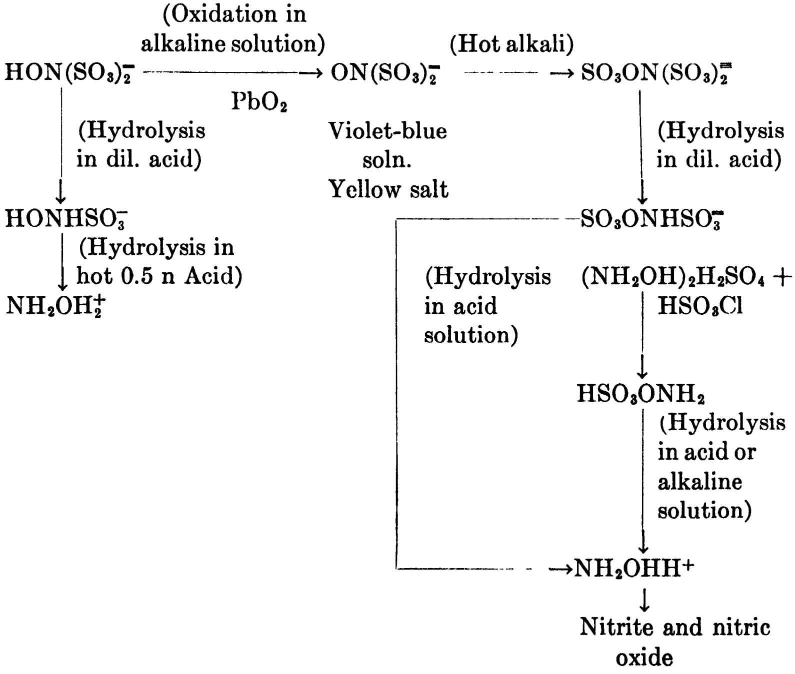
(Hydroxylamine disulfonate)

Potassium hydroxylamine isodisulfonate exists as unhydrated, colorless crystals which are soluble to the extent of 6.64 grams in 100 grams of water at 16.4°. Aqueous solutions of the salt are neutral to litmus, methyl orange, and phenolphthalein and, when made alkaline, are not affected by PbO_2, as is the normal disulfonate [see the excellent paper by Haga, *J. Chem. Soc.*, **89,** 240 (1906)]. Sodium hypochlorite oxidizes the alkaline solutions to nitrogen and some N_2O [Raschig, *Chem. Abst.*, **19,** 2176 (1925); *Chem. Zentr.*, II, 447 (1924)]. In concentrated KOH solutions at 125°, decomposition to K_2SO_4, KH_2NSO_3, and nitrogen slowly takes place. (The normal disulfonate hydrolyzes very slowly, in concentrated KOH, to nitrite and sulfite.) In acid solutions the isodisulfonates decompose to form hydroxylamine salts and sulfate together with nitric oxide, some nitrogen, and other products. Sodium amalgam reduces alkaline isodisulfonate solutions to $K[H_2NSO_3]$ but does not affect the normal disulfonate.

The hydrolysis of hydroxylamine isodisulfonate in acid solution does not lead to the isomonosulfonate $K[SO_3ONH_2]$ but to hydroxylammonium salts, sulfates, nitrites, and other products. However, when hydroxylammonium sulfate is warmed with chlorosulfonic acid, HSO_3Cl, a strongly oxidizing compound $H[SO_3ONH_2]$ is formed [Sommer, Schulz, and Nassau, *Z. anorg. Chem.*, **147,** 142 (1925)] which precipitates from the mixture and may be washed with ether. In the presence of moisture it hydrolyzes to hydroxylammonium bisulfate; in acid solutions the rate of hydrolysis is slow and in neutral or alkaline solutions the rate is measurable.

In the discussion so far only the potassium salts were described in detail; ordinarily it is these that are most readily prepared. Salts of the other alkali metals, the alkaline earths, and a number of heavy metals have been prepared and their qualitative properties described. The sodium and ammonium salts are more soluble than those of potassium; some of the lead and barium salts are only slightly soluble.

The two series of hydroxylamine sulfonates are, as indicated, interrelated, and this is more easily seen in the following schematic arrangement; for simplicity, the ions are shown when they are well known.



The principal end product of the acid hydrolysis of the hydroxylamine sulfonates is hydroxylamine or, more properly, hydroxylammonium salts. Ordinarily one works with the salts of hydroxylamine, for example, NH_2OHHCl, and only for special reasons is the so-called free base NH_2OH

isolated. The isolation of the free base is best achieved by treating the hydrochloride with sodium ethylate or butylate. To this end sodium is placed in butyl alcohol and the mixture is refluxed until the metal is dissolved. The sodium butylate formed is added slowly to a mixture of NH_2OHHCl and butyl alcohol in a closed vessel, and the resulting sodium chloride is filtered off. When the filtrate is cooled to $-10°$, large white flakes of NH_2OH separate [Hurd and Brownstein, *J. Am. Chem. Soc.*, **47,** 67 (1925)]. Because of its instability, free hydroxylamine should be kept on ice to avoid decomposition.

Free hydroxylamine, NH_2OH, melts at 33° to give a liquid of density 1.204, which, under a pressure of 22 mm, boils at 58° with some decomposition. At higher temperatures decomposition into N_2 and N_2O becomes excessive, and explosions are sometimes observed. The solid is miscible with water, methyl, and ethyl alcohols, but is insoluble in liquid hydrocarbons. It reacts with acetone [Lobry De Bruyn, *Ber.*, **27,** 968 (1894)]. Aqueous solutions containing up to 60% NH_2OH are moderately stable.

The properties of NH_2OH recall those of water, and if it is remembered that liquid NH_3 has many properties resembling those of water, it is not surprising that the substitution of an —OH group for H in NH_3 yields a compound that shows a still closer resemblance to water.

Aqueous solutions of the salts of hydroxylamine act as both oxidizing and reducing agents. Thus with trivalent titanium or bivalent chromium, hydroxylammonium salts in acid solution are reduced to ammonium salts [Bray, MacKenzie, and Simpson, *J. Am. Chem. Soc.*, **41,** 1363 (1919)]. The reducing action of hydroxylamine is shown in its reactions in acid solutions with noble metal salts (Ag, Au, Hg), the products being the metals, nitrogen, and oxides of nitrogen. Permanganate, bromine, and other oxidizing agents are reduced in acid solutions. In alkaline solution hydroxylamine slowly decomposes into nitrogen, ammonia, and to some extent N_2O. The alkaline solutions oxidize ferrous to ferric hydroxide, ammonia being the reduction product of the hydroxylamine. Cupric hydroxide is reduced to Cu_2O and N_2O is formed. The acid solutions will reduce ferric to ferrous ion, the hydroxylamine being oxidized to N_2O. The acid solutions are much more stable than are the alkaline solutions.

Hydroxylamine has also, like water and ammonia, the property of filling coordination positions in complex compounds, and such complexes are not much less stable than the corresponding ammonia compounds. The zinc hydroxylamine chloride, $Zn(NH_2OH)_2Cl_2$, can be prepared in the solid form; significant from the point of view of stability is the fact that warming under a vacuum or treatment with ammonia suffices to displace the hydroxylamine. Cobalt in the trivalent form is able to bind six hydroxylamines just as it does six ammonias. Thus

$Co(NH_2OH)_6Cl_3$ has been prepared. With nickel, the red compound $[Ni(NH_2OH)_6]SO_4$ is formed.

When free hydroxylamine is dissolved in water, the resulting solution is weakly alkaline. In this it resembles ammonia and hydrazine. The ionization constants for these three bases are as follows [Latimer, *Oxidation Potentials*, pp. 87, 89, 90; Winkelbleck, *Z. phys. Chem.*, **36,** 574 (1901); Schwarzenbach, *Helv. Chem. Acta,* **19,** 178 (1936); Ishikawa and Aoki, *Bull. Inst. Phys. and Chem. Research*, **19,** 136 (1940), report $K = 4 \times 10^{-8}$ for hydroxylamine]:

$$NH_4OH = NH_4^+ + OH^-$$

$$\frac{(OH^-)(NH_4^+)}{(NH_4OH)} = 1.81 \times 10^{-5} \qquad \text{(Ammonium hydroxide)}$$

$$NH_2OH_2OH = NH_2OH_2^+ + OH^-$$

$$\frac{(OH^-)(NH_2OH_2^+)}{(NH_2OH_2OH)} = 6.6 \times 10^{-9} \qquad \text{(Hydroxylammonium hydroxide)}$$

$$N_2H_6(OH)_2 = N_2H_6OH^+ + OH^-$$

$$\frac{(OH^-)(N_2H_6OH^+)}{(N_2H_6(OH)_2)} = 8.5 \times 10^{-7} \qquad \text{(Hydrazinium hydroxide)}$$

$$N_2H_6OH^+ = N_2H_6^{++} + OH^-$$

$$\frac{(OH^-)(N_2H_6^{++})}{(N_2H_6OH^+)} = 8.9 \times 10^{-16}$$

Amine Sulfonates

Attention has already been called to the view that hydroxylamine can be regarded as a derivative of ammonia; later it will be seen that hydrazine can be considered in a like manner. Thus the three compounds ammonia, hydroxylamine, and hydrazine would be written,

NH_3	NH_2OH	NH_2NH_2
Ammonia	Hydroxylamine	Hydrazine

The hydroxylamine sulfonates, in turn, are derivatives of ammonia in which the hydrogens are replaced by hydroxyl and sulfonate groups.

NH_3	NH_2OH	$(SO_3)_2NOH^{=}$
Ammonia	Hydroxylamine	Hydroxylamine disulfonate

Derivatives of ammonia are well known in which one, two, or three of the hydrogens are replaced by one, two, or three sulfonate groups; that is, unlike the hydroxylamine sulfonates, no hydroxyl group is present. These three compounds and their present and former names are

$N(SO_3)_3^{\equiv}$	$NH(SO_3)_2^{=}$	$NH_2(SO_3)^-$
Amine trisulfonate	Amine disulfonate	Amine sulfonate
(Nitrilosulfonate)	(Imidosulfonate)	(Amidosulfonate)

These compounds could equally well be regarded as derivatives of sulfate ion, $SO_4^=$, in which the oxygens of one or more sulfate ions are replaced by $-NH_2$, $=NH$, or $\equiv N$. The equations which show this point, but which do not necessarily represent known reactions, are

$$\begin{aligned} SO_4^= + NH_3 &= SO_3NH_2^- + OH^- \\ 2SO_4^= + NH_3 &= (SO_3)_2NH^= + 2OH^- \\ 3SO_4^= + NH_3 &= (SO_3)_3N^{\equiv} + 3OH^- \end{aligned}$$

It must be emphasized that the two ways of looking at the amine sulfonates do not necessarily add anything fundamental to our knowledge of their chemistry, but are rather memory aids or suggestions that may serve to lead to a rigorous structure determination. An X-ray investigation has shown that the amine sulfonate ion in crystals of KNH_2SO_3 has a structure similar to that of the sulfate ion with an NH_2 group in place of one O, but distorted slightly from a perfect tetrahedron. The S—N distance is 1.56 Å and the S—O distance is 1.48 Å [Ketelaar and Heilmann, *Z. Krist.*, **103,** 41 (1940)]. The hydrogens are not located by the X-ray method, but the packing of the ions is such that they undoubtedly form hydrogen bonds from the nitrogen to the oxygens of neighboring molecules.

The amine sulfonates are written in the ionic form, since the salts are the well-known and stable compounds of them; the free acids are, with the exception of amine monosulfonic acid, unstable.

Amine trisulfonate (nitrilo sulfonate) of potassium was discovered by Fremy in 1845; it is prepared by the reduction of potassium nitrite with neutral potassium sulfite at room temperature or lower [Claus and Koch, *Ann.*, **152,** 336 (1869); Divers and Haga, *J. Chem. Soc.*, **79,** 1093 (1901)]. For example, a solution of 100 g of KOH in 200–250 cc of water is treated with sulfur dioxide until the resulting solution is neutral. This solution is mixed with one containing 25 g of KNO_2 in 100 g of water. In two or three minutes a large, mushy precipitate of potassium amine trisulfonate, $K_3[N(SO_3)_3]\cdot 2H_2O$, separates; the whole mixture may eventually solidify. After standing for an hour the mixture is heated on a water bath (water is added if necessary for solution) and then allowed to cool. Beautiful, needle-like, rhombic crystals separate. The solid is not stable, and in the course of a month or so it hydrolyzes into $K_2[NH(SO_3)_2]$ and potassium bisulfate. The reaction leading to its formation is

$$NO_2^- + 3HSO_3^- = N(SO_3)_3^{\equiv} + H_2O + OH^-$$

and the hydrolytic decomposition of the salt is represented by

$$K_3N(SO_3)_3\cdot 2H_2O = K_2NH(SO_3)_2 + KHSO_4 + H_2O$$

Potassium amine trisulfonate is only sparingly soluble in cold water, about 2 g in 100 g of water at 23°, and the solutions are neutral to litmus. The sodium salt is much more soluble than this, and the complex salt $[Co(NH_3)_6]N(SO_3)_3$ is practically insoluble [Ephraim and Flügel, *Helv. Chem. Acta,* **7,** 724 (1934)]. The similarity of the reduction reaction to that involved in the formation of hydroxylamine disulfonate will be noted at once; the principal difference is that more reducing agent, HSO_3^-, is mixed with the nitrite and a higher temperature is required. This indicates that hydroxylamine disulfonate would be capable of further reduction, and, indeed, it is possible by means of zinc, Zn-Cu, or sodium amalgam to reduce it to amine disulfonate. When boiled, the solutions of the alkali metal amine trisulfonates are rapidly and irreversibly hydrolyzed to amine disulfonate and amine sulfonate.

The addition of a small amount of acid to the solutions of $K_3[N(SO_3)_3]$ at room temperature catalyzes the hydrolysis to amine disulfonate and amine sulfonate, the former being an intermediate stage. If the acid concentration is very low, the hydrolysis of the di- to monosulfonate appears to be slower than that of the tri- to disulfonate. The efforts of Wagner [*Z. phys. Chem.,* **19,** 668 (1896)] to show that the tri- to disulfonate hydrolysis is immeasurably rapid do not seem to have been entirely successful; a careful re-examination of the rates is desirable.

Potassium amine disulfonate (imidosulfonate) is prepared by moistening the crystals of the trisulfonate with very dilute acid and allowing to stand for a day. After washing, the salt is recrystallized from dilute ammonia solution. The resulting small, colorless crystals of $K_2[NH(SO_3)_2]$ are not very soluble in water, 1.56 g in 100 g water at 23°, and the fresh solutions are practically neutral [Raschig, *Ann.,* **241,** 171 (1887)]. The ammonium salt $(NH_4)_2[NH(SO_3)_2]\ NH_3$ is formed directly in the reaction between gaseous ammonia and sulfur trioxide.

$$4NH_3(g) + 2SO_3(g) = (NH_4)_2[NH(SO_3)_2]\cdot NH_3(s)$$

In neutral and basic solutions the amine disulfonates are stable at room temperatures, but boiling brings about hydrolysis to the monosulfonate. With warm sodium hypochlorite solutions, the amine disulfonate reacts to form the explosive compound chloraminedisulfonate, $K_2[ClN(SO_3)]_2$; this reaction recalls that between chlorine and ammonia to form chloramine, NH_2Cl. The explosive property is due to the decomposition into $K_3N(SO_3)_3$ and NCl_3, the latter substance being violently explosive.

The amine disulfonates in dilute acid solution hydrolyze at a measurable rate at room temperatures to the amine sulfonates.

$$NH(SO_3)_2^{=} + H_2O = NH_2SO_3^- + H^+ + SO_4^{=}$$

The hydrolysis is catalyzed by hydrogen ion, and the rate appears to be directly proportional to the concentration of both H^+ and $NH(SO_3)_2^{=}$;

the few measurements reported by Wagner (*loc. cit.*) are so expressed that it is not possible to determine the units used for expressing the rate constants.

The solid salt $K_2NH(SO_3)_2$ is stable at room temperature, as are also other alkali and alkaline earth salts, but they decompose on heating to some 200°. The complex cobalt salt $[Co(NH_3)_6]_2(NH(SO_3)_2)_3$ is quite insoluble (Ephraim and Flügel, *loc. cit.*). $K_2NH(SO_3)_2$ is more soluble in KOH solutions than in water, owing to the neutralization of the remaining hydrogen; salts of the formula $K_3N(SO_3)_2 \cdot H_2O$ are known which give off water at 100° but do not otherwise decompose even at 200°. Permanganate does not oxidize the alkaline solutions of the disulfonates. When silver nitrate is treated with a solution of the disulfonate (the sodium salt, being very soluble, is to be preferred for solution experiments to the rather insoluble potassium salt), a precipitate of $Ag_3N(SO_3)_2$ is formed which dissolves on addition of an excess of the disulfonate. From the resulting solution, crystals of the only moderately soluble $NaAg_2N(SO_3)_2$ and $Na_2AgN(SO_3)_2$, depending on the relative amount of disulfonate added, separate out. The acid character of the ammonia hydrogen is shown by liquid ammonia itself, where it ionizes slightly into H^+ and NH_2^-; the sodium silver salt is another illustration of this tendency in the derivatives of ammonia.

The last member of the series of amine sulfonates, also known as amidosulfonate or sulfamic acid, is the most stable of all; it results from the hydrolysis of the tri- and disulfonates (compare hydroxylamine monosulfonate). The potassium salt, KNH_2SO_3, may be prepared by boiling an aqueous mixture of the tri- or disulfonate of potassium. The free sulfuric acid formed is neutralized with calcium carbonate, and, after filtering, the less soluble K_2SO_4 is crystallized out by evaporating the solution. Eventually KNH_2SO_3 crystallizes from the concentrated and viscous solution as beautiful, colorless crystals [Raschig, *Ann.*, **241,** 176 (1887); see also Berglund, *Ber.*, **9,** 1896 (1876), and Divers and Haga, *J. Chem. Soc.*, **69,** 1634 (1896)]. Owing to their importance, a number of methods for the preparation of amine sulfonates have been developed. When urea, NH_2CONH_2, is dissolved in concentrated sulfuric acid and the resulting solution treated with fuming sulfuric acid, the reaction

$$H_2NCONH_2 + H_2SO_4 + SO_3 = 2HNH_2SO_3 + CO_2$$

takes place. The product precipitates from the reaction mixture and is recrystallized from water [Cupery, *Ind. Eng. Chem.*, **30,** 627 (1938); see also the review by Audrieth, Sveda, Sisler, and Butler, *Chem. Rev.*, **26,** 49 (1940)]. This method gives good yields, and the reactants are readily obtainable. In another method a solution of hydroxylamine sulfate (16.5 g) in water (50 g) is cooled to −80° and excess sulfur dioxide is allowed to condense on it. On allowing this mixture, in a sealed container, to stand for fifteen or twenty hours at about 25°, the solid HNH_2SO_3 crystallizes out. The pressure of SO_2 reaches 3.5 to 4 atm above $SO_2(l)$. The yield can reach 70% [Sisler and Audrieth, *J. Am. Chem. Soc.*, **61,** 3389 (1939)].

Potassium amine sulfonate is readily soluble in water but insoluble in alcohol, and its aqueous solutions are slightly alkaline to litmus but not to phenolphthalein. Its solutions do not hydrolyze readily at room temperature; but if heated in a closed tube with hydrochloric acid to 140°, or boiled with hydrochloric acid for several hours at atmospheric pressure, the salt is converted eventually to ammonium and sulfate ions.

$$NH_2SO_3^- + H_2O = NH_4^+ + SO_4^=$$

In acid solutions this hydrolysis takes place only very slowly at room temperature. Unlike the amine tri- and disulfonates, the free acid of the monosulfonate, NH_2SO_3H, is stable and can be prepared in the solid unhydrated form. It may be crystallized from acid solutions of its salts, or it may be prepared by passing SO_2 into aqueous solutions of hydroxylamine hydrochloride,

$$NH_2OH_2^+ + Cl^- + H_2SO_3 = 2H^+ + NH_2SO_3^- + Cl^- + H_2O$$

or by either of the two methods described above. The free acid is soluble in water and may be crystallized from its solutions without much difficulty in the anhydrous form; it is appreciably soluble in methyl and ethyl alcohols, slightly so in acetone, but is insoluble in ether; in liquid ammonia it is very soluble. The solubility is said to be low in H_2SO_3 solutions. In sulfuric acid the solubilities in 100 g of solvent at 30° are as follows:

Per Cent H_2SO_4	Solubility HNH_2SO_3, g per 100 g Solvent
0.0	14.68(0°) 26.09 47.08(80°)
23.91	4.14
47.53	1 06
71.80	0.00
81.17	0.25
Fuming (21.1 % SO_3)	2.38

The anhydrous acid is quite stable at room temperatures; and because of this fact and the ease with which it can be prepared in pure form, it has been suggested as a primary standard in acidimetry. That this suggestion has merit is shown by the results of Audrieth and coworkers [Butler, Smith, and Audrieth, *Ind. Eng. Chem., Anal. Ed.*, **10,** 690 (1938)], who found that a product fractionally recrystallized from warm water was 99.945% pure as determined by titration with carefully standardized barium hydroxide. Bromothymol blue changes sharply from yellow to blue at the equivalence point. NH_2SO_3H melts with decomposition at 205°.

Amine sulfonic acid is a strong acid. Conductivity measurements show the percentage degree of ionization to be 98% at 0.001 m and 79% at 0.03 m at 25° [Sakurai, *J. Chem. Soc.*, **69,** 1654 (1896); Winkelbleck, *Z. phys. Chem.*, **36,** 546 (1901)]. Solutions of the acid and its salts are not readily oxidized at room temperature; in boiling alkaline solutions, silver oxide is reduced to metallic silver, and sulfite and nitrogen are the oxidation products. With hypochlorous acid, cold solutions of the potassium salt yield solutions of $KNHClSO_3$, and this may be precipitated by the addition of alcohol to concentrated aqueous solutions of the salt. $KNHClSO_3$ is hydrolyzed by warm, strong acids to sulfuric acid and chloramine, NH_2Cl. Acid solutions of NH_2SO_3H are rapidly and quantitatively oxidized to nitrogen by KNO_2; concentrated HNO_3 reacts to form good yields of N_2O. In neutral or acid solutions of amine sulfonates, silver nitrate produces, under the proper conditions of concentration, a precipitate of $AgNH_2SO_3$, a salt which is moderately soluble in water (6.7 g per 100 g H_2O at 19°). The addition of potassium hydroxide to the solutions of the silver salt gives rise to a yellow precipitate of $KAgNHSO_3$; that is, the ammonia hydrogens have a weakly acidic character. The barium salt, $Ba(NH_2SO_3)_2$, is soluble in water to the extent of 34.2 g per 100 g of water at 25°.

Amine sulfonate ion, $NH_2SO_3^-$, is capable of coordinating with bivalent platinum. Thus when K_2PtCl_4 is treated with NH_2SO_3H solutions, a soluble and a sparingly soluble platinum complex are formed, namely, cis and trans $K_2[PtCl_2(NH_2SO_3)_2]$, respectively, the cis being the soluble form. Both of these salts dissolve in potassium hydroxide solution to form tetrapotassium salts, $K_4[PtCl_2(NHSO_3)_2]$ [Kirmreuther, *Ber.*, **44,** 3115 (1911)]. The amine sulfonate groups in the complexes are readily replaceable by pyridine. Complex cobalt amine salts, for example, $[Co(NH_3)_6](NH_2SO_3)_3 \cdot 2H_2O$, have been prepared; this salt, unlike the corresponding amine disulfonate, is moderately soluble in water, 1.46 g per 100 g solution.

The properties of the three amine sulfonates can be summarized as follows: The solubilities of the potassium salts increase with decrease in number of sulfonate groups; they hydrolyze to form the lower sulfonates, the rate of hydrolysis being greater the larger the number of sulfonate groups; they are not oxidized or reduced rapidly at room temperature;

the neutrality or near neutrality of fresh solutions of the salts show them to be salts of strong acids; the hydrogens attached to the nitrogen in the di- and monosulfonates are weakly acid in character and may be neutralized with strong bases.

Sulfamide and Imidosulfamides

The amine and hydroxylamine sulfonates are the best-known examples of a large class of derivatives of ammonia. In organic chemistry these derivatives include a large group of compounds which play an important role in life processes. Very often the organic compounds are more stable toward hydrolysis and the action of reagents than are the inorganic derivatives. The inorganic substances have not been extensively investigated; therefore, it must suffice here to give a rather brief account of their preparation and properties.

When ammonia is passed into a chloroform or benzene solution of SO_2Cl_2, there are formed sulfamide, $(NH_2)_2SO_2$, sulfimide, $(NHSO_2)_3$, and imidosulfamide, $NH(NH_2SO_2)_2$, the relative amounts of the products depending on experimental conditions [Hantzsch and Stuer, *Ber.*, **38,** 1022 (1905); Ephraim and Michel, *Ber.*, **42,** 3833 (1909); Hantzsch and Holl, *Ber.*, **34,** 3430 (1901)]. The reactions are

$$\begin{aligned} 2NH_3 + SO_2Cl_2 &= (NH_2)_2SO_2 + 2HCl \\ 3NH_3 + 2SO_2Cl_2 &= NH(NH_2SO_2)_2 + 4HCl \\ 3NH_3 + 3SO_2Cl_2 &= (NHSO_2)_3 + 6HCl \end{aligned}$$

It was found by Ephraim and Gurewitsch [*Ber.*, **43,** 138 (1910)] that a much better yield could be obtained by slowly adding SO_2Cl_2 (l) to liquid ammonia at −75°. The main product formed is imidosulfamide, and it is not very soluble in liquid ammonia. After adding the required amount of SO_2Cl_2, the excess ammonia is evaporated, and the residue is dissolved in water. The aqueous solution is made slightly acid and allowed to stand 48 hours, when the hydrolytic reaction to form sulfamide is completed.

$$NH(NH_2SO_2)_2 + 2H_2O = (NH_2)_2SO_2 + NH_4^+ + H^+ + SO_4^=$$

The aqueous solution is evaporated at 50° under a vacuum and the residue is extracted with ethyl acetate, in which only the sulfamide is soluble. The sulfamide may be recrystallized from ethyl acetate, glycol monoethyl, or hot ethyl alcohol as large, colorless, rhombic crystals which are tasteless but have a cooling sensation on the tongue.

Sulfamide melts at 93°, where its density is 1.611 g/cm^3 and the surface tension $\gamma = 72.35$ dynes/cm; above the melting point decomposition sets in with the formation of ammonia and sulfimide. At still higher temperatures, 250°, complete decomposition into ammonia and sulfur acids appears to take place. Sulfamide is readily soluble in water to form very faintly acid solutions ($\Lambda = 30$ ohm^{-1} at .001 m); on addition of ammonia and silver nitrate, a precipitate of $Ag_2(NH)_2SO_2$ forms which is soluble in acid. These facts indicate the weakly acid character of sulfamide, and the nature of the salt recalls that of analogous compounds of amine and hydroxylamine sulfonates in which a hydrogen attached directly to nitrogen is capable of ionizing slightly. The reaction between sulfamide and metallic potassium in liquid ammonia yields two potassium salts similar to the above-noted silver salt.

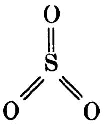
Boiling acids bring about the hydrolysis of sulfamide to ammonium sulfate; with alkalies, amine sulfonic acid salts are the hydrolytic products, for example, $K[NH_2SO_3]$. With cold nitrous acid solutions, sulfamide is oxidized to nitrogen and sulfuric acid. Cold, concentrated nitric acid does not react with sulfamide, but the addition of concentrated sulfuric acid to the nitric acid solution yields an explosive precipitate of $NH_2SO_2NHNO_2$.

Sulfamide is capable of acting as a coordinating group or addendum in some complex compounds, and in so doing it occupies two coordination positions, as might be expected, since the molecule has at least two if not three polar groups in it. Thus the very stable free acid $H[Rh(H_2O)_2(SO_2(NH)_2)_2]$ has been prepared by Mann [*J. Chem. Soc.*, 412 (1933)]. It may be heated to 300° without decomposition and is insoluble in water. The sodium salt of the complex has been resolved into its optically active isomers; their molal rotation is $[M]_{5780} = 31°$.

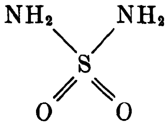
Imidosulfamide, $NH(NH_2SO_2)_2$, appears to exist as such and as still longer chains, namely, $NH_2SO_2NHSO_2NHSO_2 \ldots NHSO_2NH_2$. It acts as a very weak acid of which the silver salts are best known (Ephraim and Gurewitsch, *loc. cit.*). The mixture of imidosulfamide and the longer chains are the first and main products of the action of SO_2Cl_2 on liquid ammonia.

Sulfimide, which is not so well known as the sulfamide and imidosulfamide, is formed in the reaction of ammonia with chloroform or benzene solutions of sulfuryl chloride, and by heating sulfamide at or a little above the melting point. The formula in solution seems to be $(NHSO_2)_3$. The silver salt is said to be insoluble in alkaline and neutral solutions, and this distinguishes it from the corresponding silver sulfamide, which is insoluble only in alkaline solutions.

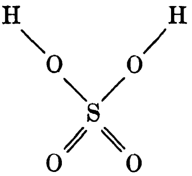
Sulfamide and the related compounds may be regarded as derivatives of ammonia, or alternatively as derivatives of sulfur trioxide in the same sense that the amine sulfonates are derivatives of sulfuric acid. Indeed, the alkaline hydrolysis of sulfamide leads directly to amine monosulfonate.



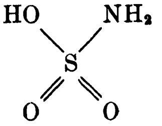
Sulfur trioxide



Sulfamide



Sulfuric acid



Amine monosulfonic acid

Amine Sulfinic Acids

When sulfur dioxide and ammonia gas are mixed, white solids form which contain the ammonium salts of the mono- and disulfinic acids. Thus,

$2NH_3 + SO_2 = NH_4(NH_2SO_2)$ (Ammonium amine monosulfinite)
$4NH_3 + SO_2 = (NH_4)_2(NH(SO_2)_2)$ (Ammonium amine disulfinite)

The amine sulfinites may be regarded as derivatives of sulfurous acid in the same sense that the amine sulfonates are derivatives of sulfuric acid.

The reaction between ammonia and thionyl chloride, $SOCl_2$, yields the anhydrides of the amine sulfinic acids. Thus,

$$3NH_3 + 2SOCl_2 = NH_2SONHSONH_2 + 4HCl$$

The hydrolysis of this compound leads to amine sulfinites in a manner recalling the hydrolysis of sulfamide to amine sulfonic acid.

Nitramide, NH_2NO_2

So far we have concerned ourselves principally with ammonia derivatives containing sulfur-oxygen groups. The main reason for this is that these compounds are numerous and are easily prepared and studied. Nitramide may be regarded as a derivative of nitric acid, $HONO_2$, in which the —OH group is replaced by its analogue —NH_2. It has not been prepared by the action of nitryl chloride, NO_2Cl, on ammonia, but it seems reasonable to suppose that it could be. Ordinarily the preparation is accomplished by the hydrolysis of $NO_2NHCOOK$ with concentrated sulfuric acid, the resulting mixture being then saturated with ammonium sulfate and extracted with ether. The ether solution is evaporated, and the residue is dissolved in absolute alcohol, from which the nitramide is precipitated by the addition of chloroform or ligroin. The nitramide is obtained as white, shining plates which melt and immediately decompose at 72–75°.

Aqueous solutions of nitramide are weakly acidic, the ionization constant being

$$\frac{(H^+)(NHNO_2^-)}{(NH_2NO_2)} = 2.55 \times 10^{-7} \text{ at } 15^\circ$$

[Bronsted and King, *J. Am. Chem. Soc.*, **49**, 200 (1927)]. This acidic character results from the weakly acid properties of ammonia itself ($NaNH_2$ and Ca_3N_2 are known salts); this property is augmented by the presence of a substituted group. Aqueous solutions of nitramide are not stable; they decompose slowly according to the equation

$$NH_2NO_2 = N_2O + H_2O$$

In alkaline solution the rate of decomposition is very rapid, but in acid solution it is measurably slow [Marlies and LaMer, *J. Am. Chem. Soc.*, **57**, 1812 (1935)]. The rate of decomposition in hydrochloric acid solution depends to a small extent on the concentration, C_{HCl}, of acid.

$$-\frac{d(NH_2NO_2)}{dt} = k(NH_2NO_2)$$

$$k = 1.235 \times 10^{-3} + 0.328 \times 10^{-3}C_{HCl} \text{ at } 24.84°$$

The fact that the rate is much more rapid in alkaline than in acid solution suggests that $NHNO_2^-$ is more unstable than the un-ionized nitramide. This property differs from that observed with the ammonia derivatives discussed in the preceding sections in that they decompose more rapidly in acid than in alkaline solution. The small amount of acid catalysis observed in the case of nitramide indicates still another unstable species such as $NH_3NO_2^+$.

It will be noted that nitramide is isomeric with hyponitrous acid, $H_2N_2O_2$. Hyponitrous acid is about equal in strength ($K = 9 \times 10^{-8}$) to nitramide, but in contrast with the latter it decomposes rapidly in acid solution. Nitramide is a derivative of ammonia, while hyponitrous acid has the structural formula HONNOH, although the molecule is doubtless not linear. The decomposition of hyponitrous acid yields nitrous oxide and water just as that of nitramide does, but un-ionized $H_2N_2O_2$ decomposes much more rapidly than does un-ionized NH_2NO_2. Hyponitrite ion $N_2O_2^=$ decomposes much less rapidly than does nitramide ion $NHNO_2^-$.

Ammonia Derivatives of Phosphorus Oxyacids

The reaction between phosphorus pentoxide and ammonia is believed to lead to the amine and diamine phosphoric acids. However, these reactions have not been thoroughly investigated, and our knowledge of the amine phosphoric acids comes mainly from the substances prepared by the hydrolysis of phenyl dichlor and diphenyl chlor phosphoric acid [Stokes, *Amer. Chem. J.*, **15**, 198 (1893); **20**, 740 (1898)].

$$OClP(OC_6H_5)_2 + NH_3 + 2H_2O = H_2[PO_3NH_2] + 2C_6H_5OH + HCl$$

$$OClPOC_6H_5 + 2NH_3 + H_2O = H[PO_2(NH_2)_2] + C_6H_5OH + 2HCl$$

The same compounds are formed by the action of ammonia on the phosphorus oxychlorides, $POCl_3$ and PO_2Cl. Both the amine and diamine phosphoric acid exist as such and are soluble in water but not in alcohol; the former is dibasic, while the latter is both monobasic and even pentabasic. Amine phosphoric acid forms both normal and acid salts. Accordingly, the second hydrogen of $H_2[PO_3NH_2]$ ionizes less readily than does the first. The ability of the diamine to form higher salts is due, as in the amine and hydroxylamine sulfonates, to the weakly acidic character of the ammonia hydrogens.

Amine and diamine phosphoric acids hydrolyze slowly in water to yield, eventually, ammonium hydrogen phosphate. The rate of hydrolysis is more rapid in hot than in cold water and is greater in alkaline than in neutral solutions.

The action of ammonia gas on a benzene or ether solution of phosphorous oxide, P_4O_6, brings about the formation of diamine phosphinic acid, $H[PO(NH_2)_2]$ [Thorpe and Tutton, *J. Chem. Soc.*, **59**, 1027 (1891)]. This substance dissolves in water with great violence and with decomposition into ammonium phosphites, phosphates, and phosphorus.

Other ammonia derivatives of the phosphorus acids are known, for example, $H[OPOHNH]$, $OPNHNH_2$, OPN, $O_3P_2OH(NH_2)_3$, and $HNP_2O_2NH(NH_2)_2$. Thiophosphoric acid derivatives are also known, for example, $PS(NH_2)_3$.

Phosphorus Chloronitrides, $(PNCl_2)_n$

When an equimolal mixture of PCl_5 and NH_4Cl are heated together in a closed tube at 150°, a remarkable series of compounds is formed whose general formula is $(PNCl_2)_n$, where $n = 3, 4 \cdots 7$ and higher. The general reaction may be written

$$n\ PCl_5 + n\ NH_4Cl = (PNCL_2)_n + 4n\ HCl\ (g)$$

Two methods of preparation have been developed. In the first, discovered in its essentials by Liebig (1834) and examined in detail by Stokes [*Am. Chem. J.*, **19**, 782 (1897); see also Schenck and Römer, *Ber.*, **57**, 1343 (1924), **60**, 160 (1927)], the mixture of the two solid reagents is heated in a closed glass tube to 150° and cooled to 100°, when the tube is opened to allow the hydrogen chloride to escape. This operation is repeated several times until the contents of the tube have a buttery or thick, yellowish, liquid appearance. The material obtained is fractionally distilled at about 13–17 mm pressure, and is then recrystallized from benzene to separate the constituent compounds. In the second and more convenient method (Schenck and Römer, *loc. cit.*), a mixture of NH_4Cl (130 g) and PCl_5 (400 g), dissolved in tetrachloroethane (1 liter), $C_2H_2Cl_4$ (b.p. 146.3°), is refluxed for about seven hours or until the reaction is complete. After cooling and filtering, the solvent is distilled off at 50° and 11 mm, and the residue is subjected to fractional distillation and recrystallization from benzene as before.

The mixture obtained from the distillation in either case consists of about 50% $(PNCl_2)_3$ and 25% $(PNCl_2)_4$ together with higher polymers and small amounts of a definite compound, $P_6N_7Cl_9$. If the mixture is heated to 250°, a slow further polymerization occurs which becomes very rapid if the temperature is raised to 350°; the resulting product, when cooled to room temperature, is an elastic, colorless, transparent, rubber-like substance which is insoluble in and is not wetted by water. [For physical properties and X-ray studies, see Myer, Lotmar, and Pankow, *Helv. Chim. Acta*, **19**, 930 (1936).] Neutral solvents do not dissolve the elastic solid, but it absorbs benzene freely and in so doing swells eventually to four times its original volume. On evaporating the absorbed benzene, the substance returns to practically its original consistency. If the rubber-like polymer, known as polyphosphorus chloronitride, is heated to somewhat above 350°, slow depolymerization sets in, and this reaction becomes rapid at nearly red heat. From the conditions for polymerization and depolymerization it is evident that the reaction

$$(PNCl_2)_x = (PNCl_2)_{n_1} + (PNCl_2)_{n_2} + \cdots$$

is reversible; at 350° and below equilibrium lies to the left, and above 350° progressively to the right. The slowness of the polymerization reactions below 250° makes possible the isolation of $(PNCl_2)_3 \ldots (PNCl_2)_7$. Lower polymers have not been isolated, although they are believed to exist as intermediates in some polymerization reactions [see Ficquelmont, *Compt. rend.*, **204**, 867 (1937)]. The reversibility of the polymerization reactions and their slowness at lower temperatures makes it possible to convert all of the material to any one of the several known polymers.

The thick yellow liquid or butter-like mixture of the polymers as first prepared may be clarified by heating with water for about two hours, since it does not dissolve in water and hence hydrolysis is very slow.[1] The clarified product is fractionally distilled at low pressures; at 13–15 mm some 70% is recovered as $(PNCl_2)_3$ and $(PNCl_2)_4$, which may be separated from each other by fractional crystallization from benzene. The higher polymers distill over at still higher temperatures. Determinations of the molecular weights of the well-defined polymers have been made in boiling benzene, in which solvent all are soluble.

In the following table are presented the data on the physical properties of the well-defined polymers $(PNCl_2)_n$; solubilities are expressed in grams per 100 grams of solvent.

---

[1] If ether is added to the water, the aqueous layer wets the polymer mixture and progressive hydrolysis to hydroxy derivatives of the types $P_3N_3Cl_4(OH)_2$ and $(NHPOOH)_3$ occurs.

TABLE 24
PHYSICAL PROPERTIES OF THE PHOSPHORUS CHLORONITRIDES

Compound*	Melting Point (°C)	Boiling Point (°C)		Solubility at 20°C in			Density
		at 13 mm	at 760 mm	benzene	ether	CCl_4	
$(PNCl_2)_3$	114	127	256	55.0	46.4	38.88	1.98
$(PNCl_2)_4$	123.5	188	328.5	21.4	12.3	16 5	2 18
$(PNCl_2)_5$	41	224	polymerizes	miscible	miscible in ether, C_6H_6, CS_2	—	—
$(PNCl_2)_6$	91	262	polymerizes	soluble	—	—	—
$(PNCl_2)_7$	−18	293	polymerizes	soluble	—	—	—

* $P_6N_7Cl_9$ melts at 237°, boils at 251–261° (13 mm), and is soluble in benzene and gasoline.

The boiling points of the lower phosphorus chloronitrides increase with increase in molecular weight, but the melting points of $(PNCl_2)_5$ and $(PNCl_2)_7$ are markedly lower than those of the other members of the series. This indicates that the symmetries (symmetry numbers) of $(PNCl_2)_5$ and $(PNCl_2)_7$ are less than those of the other members. The insolubility in water and the solubility in the nonpolar solvents suggest that all of the $(PNCl_2)_n$ are nonpolar, and the manner in which the melting temperatures vary points to ring structures for these compounds. An X-ray crystal structure study [Ketelaar and de Vries, *Rec. trav. chim.*, **58,** 1081 (1939)] has proved the ring structure for $(PNCl_2)_4$ and has given the distances P—N = 1.68 Å, P—Cl = 2.00 Å and ∠PNP = 123°, ∠NPN = 117°, and ∠ClPCl = 105°30′. Electron-diffraction experiments indicate the structure of $(PNCl_2)_3$ shown in Fig. 19 (unpublished data of Dr. Verner Schomaker). [See also the recent review by Audrieth, Steinman, and Joy, *Chem. Rev.*, **32,** 109 (1943).]

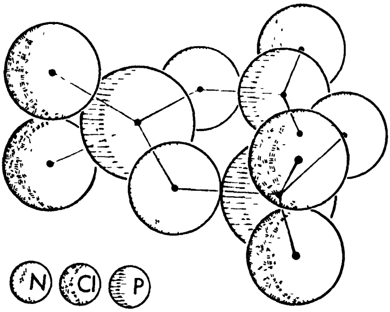


Fig 19. The Molecular Structure of $(PNCl_2)_3$. P—N ≃ 1.6Å; P—Cl = 2.04Å; ∠Cl—P—Cl ≃ 100°; ∠P—N—P ≅ 120°.

From what has been said about the symmetries of the members of the series, it seems likely that the structures of $(PNCl_2)_5$ and $(PNCl_2)_7$ are also rings, since rings containing five or seven P or N atoms will not have as high a symmetry as rings containing three, four, and six of these atoms The structure of $(PNCl_2)_6$ should be the most symmetrical of all, and this is indicated by its comparatively high melting point—that is, high compared to the members of the series immediately preceding or following it.

As already remarked, the series of well-defined phosphorus chloronitrides reacts only slowly even with boiling water. $(PNCl_2)_4$ appears to be more stable than $(PNCl_2)_3$ with respect to hydrolysis. The rate of hydrolysis can be greatly increased by the addition of a little ether to the water; this brings about a wetting action and hydrolysis proceeds, as would be expected, to hydroxy derivatives of the type $(PN(OH)_2)_n$ or, as more commonly written, $(NHPOOH)_n$. The salts $Na_3(HNPOO)_3 \cdot 4H_2O$ and $Na_4(HNPOO)_4 \cdot 2H_2O$ have been prepared which indicate the acidic character of $(NHPOOH)_3$ and $(NHPOOH)_4$. If these compounds are considered derivatives of metaphosphoric or phosphoric acid, and if we recall the similarity of $N\equiv$, $HN=$, and $H_2N—$ groups to oxygen or hydroxyl groups, then it is reasonable to expect $(HNPOOH)_3$ to have an acidic character, since it contains groups similar to those in phosphoric acid. The hydrolysis of $(PNCl_2)_3$ (and doubtless other polymers) takes place in steps, it being possible to prepare both $P_3N_3Cl_4(OH)_2$ and $(PN(OH)_2)_3$. The hydroxy derivatives $(NHPOOH)_n$ are known as phosphinic acids; their molecular structures are doubtless the same as those of the chlorides from which they are derived. The products of hydrolysis (and ammonolysis) of the phosphorus chloronitrides have been extensively investigated recently by Ficquelmont [*Ann.*, **12**, 169 (1939)]. At most, only half of the hydrogens in $(HNPOOH)_3$ and in $(HNPOOH)_4$ are replaceable. Both the salts and the free acids can be prepared in the hydrated and anhydrous forms.

The hydrolysis of $(PNCl_2)_n$ can be carried still further by treatment with alkalies. Whereas hydrolysis in an ether-water solution leads to the phosphinic acids, the hydrolysis in ammoniacal alcohol, strong alkalies, or concentrated sulfuric acid leads to ammonia and orthophosphate. This fact is made use of in the analytical methods used for the determination of the composition of $(PNCl_2)_n$. In place of hydrolysis, ammonolysis is also possible. Thus treatment of $(PNCl_2)_3$ with ammonia alone leads to $P_3N_3Cl_4(NH_2)_2$ and $P_3N_3Cl_2(NH_2)_6$, and on heating these are decomposed to $P_3N_3Cl_2(NH)_2$ and $P_3N_3(NH)_3$ (phospham), respectively; when either of the two latter compounds is heated in a vacuum at 400°, phosphorus nitride, P_3N_5, is formed. This end product of deammonation of an ammonolytic product of $(PNCl_2)_3$ is the analogue of P_4O_{10}. $P_3N_3Cl_4(NH_2)_2$ is soluble in ether, 65 g, dioxane, 48 g, and benzene, 1.5 g per 100 g of solvent at 20°; it is only slightly soluble in CCl_4 and CS_2.

The substitution of part, but not all, of the chlorine in $(PNCl_2)_4$ by fluorine in a somewhat indirect manner has been accomplished by

Schmitz-Dumont and Külkens [*Z. anorg. Chem.*, **238,** 189 (1938)]. They obtained $P_4N_4Cl_2F_6$ by heating a mixture of $(PNCl_2)_3$ (25 g) and PbF_2 (100 g) at 130–340° in an atmosphere of nitrogen. It is interesting that a derivative of $(PNCl_2)_4$ rather than one of $(PNCl_2)_3$ is the result. The physical properties of $P_4N_4Cl_2F_6$ were examined more thoroughly than has been the case with the chloronitrides, and they are shown in the following table.

TABLE 25
PHYSICAL PROPERTIES OF $P_4N_4Cl_2F_6$

Melting Point (°C)	Boiling Point (°C)	Density at 13.5°	Heat of Vaporization (cal/mole)	Trouton's Constant (cal/deg)
−12.1	105.8	1.8742	8,750	23 07

$$\text{Vapor pressure, } \log_{10} p_{\text{mm}} = -\frac{1911}{T} + 7.923$$

Molecular Weight of Vapor				Formula Weight $P_4N_4Cl_2F_6$
Temp. (°C).............	140	207	302	365
Mol. wt.................	363.5	298.5	206	

$P_4N_4Cl_2F_6$ is a colorless liquid with little odor which hydrolyzes slowly with water to form hydrochloric, hydrofluoric, and phosphinic or phosphoric acids. When heated for 17 hours in a metal bomb under pressure at 300°, a colorless rubber-like polymer (at room temperature) is formed. This polymer depolymerizes if heated mildly in the open, and it is less stable than the corresponding phosphorus chloronitride rubber.

The apparent molecular weight of the vapor decreases with increase in temperature and this points to a decomposition into simpler substances. A decomposition according to what might seem a reasonable reaction

$$3P_4N_4Cl_2F_6 = 3P_3N_3F_6 + (PNCl_2)_3$$

would lead to a value higher than 206 for the apparent molecular weight. It appears, then, that some simpler chloro-fluoro nitrides are present in the vapor state at 300°. Schmitz-Dumont and Külkens suggest that the reaction is $P_4N_4Cl_2F_6 = 2P_2N_2ClF_3$, which would result in an apparent molecular weight of 183, a value that would agree with experiment if it were assumed that the decomposition is not quite complete. Since phosphorus halogenonitrides with less than three phosphorus atoms are not known, it is desirable that the decomposition reaction be studied further.

Phosphorus bromonitrides having the formulas $(PNBr_2)_3$ and $(PNBr_2)_n$ are also known. Their preparation parallels that of the chloronitrides; phosphorus pentabromide is treated with ammonia [Besson, *Compt. rend.*, **143**, 37 (1906)]. Efforts to prepare the chloronitrides of antimony and tin have not been successful.

Hydrazine, N_2H_4

Hydroxylamine may be regarded as a hydroxy derivative of ammonia, and hydrazine in turn may be looked upon as an amide of ammonia.

H_2NH	H_2NOH	H_2NNH_2
Ammonia	Hydroxylamine	Hydrazine

The $—NH_2$ group plays the same role, as it frequently does in other compounds, in hydrazine as the —OH group does in hydroxylamine. The fact that the two nitrogens are bonded to each other suggests also an analogy with hydrogen peroxide,

$$HO—OH \qquad H_2N—NH_2$$

and, indeed, the properties of hydrazine parallel those of hydrogen peroxide in several respects.

Hydrazine appears in small amounts as a reduction product in a number of reactions involving nitrates, nitrites, and other nitrogen compounds. The method of preparation now used depends, however, on the oxidation of ammonia in alkaline solution by hypochlorite [discovered by Raschig, *Ber.*, **40**, 4588 (1907)]. In order that the yield be appreciable, it is necessary that the reaction mixture contain glue or gelatine, the function of which has not been definitely established. The first step in the reaction is thought to be the formation of chloramine, NH_2Cl,

$$NH_3 + ClO^- = NH_2Cl + OH^-$$

then

$$NH_2Cl + NH_3 = N_2H_4 + HCl$$

That the glue or gelatine does not form a compound with chloramine is shown by the fact that the distribution ratio between ether and water or water containing glue and ammonia is the same [Joyner, *J. Chem. Soc.*, **123**, 1114 (1923)].

$R = \frac{\text{NH}_2\text{Cl (ether layer)}}{\text{NH}_2\text{Cl (aqueous layer)}}$	Aqueous Layer
1.4	Water at 0°
1.5	Glue soln. at 0°
1.3	Water at −8°
1.3	2 n NH_3 at −8°
1.4	2 n NH_3 + glue at −8°

It is still possible for glue or gelatine to act catalytically without at the same time forming with NH_2Cl a compound present at detectable concentrations.

The effect of the glue or gelatine and the relative concentrations of ammonia and hypochlorite on the yield has been determined carefully by Joyner (*loc. cit.*); representative data are shown in the following table.

TABLE 26

THE EFFECT OF CATALYST AND CONCENTRATIONS ON THE YIELD OF HYDRAZINE

10 cc 3.95 n NaClO + 1 cc 10% glue soln. mixed with varying amounts of 7.95 n NH_4OH, and the mixture diluted to 100 cc and heated at 80–90°.			Mixture 0.4 n in NH_4OH and 0.01 m in NaClO heated to 80-90°.	
Moles NH_4OH in 100 cc	Mole Ratio (NH_3/NaClO)	Per Cent Yield Based on NaClO	Milligrams Gelatine per 100 cc Mixture	Per Cent Yield Based on NaClO
0.0397	2.02	5.7	0	2.0
.0795	4.04	18	1.9	8.8
.1590	8.08	32	2.9	18.2
.3925	20.2	52	3.9	25.4
.7155	36.4	63	10.9	39.0
1.510	76.8	75	30.9	48.3
			100.9	51.0

The presence of NH_4^+ greatly decreases the yield; for best results, the solution should be alkaline with NaOH. Ordinarily one prepares the mixture by passing the proper amount of chlorine into a sodium hydroxide solution and then adding the most effective amount of strong ammonia solution and some glue or gelatine. The resulting mixture is heated to 80–90° for from one-half to one hour; it is then cooled and neutralized with sulfuric acid. $N_2H_6SO_4$ crystallizes out, since it is not very soluble in water and is less so in solutions containing sulfate ion.

A less convenient method for preparing hydrazine, but one which is of chemical interest, is that of Divers and Haga [*J. Chem. Soc.*, **69**, 1610

(1896)]. The salt $K_2[(NO)_2SO_3]$ is first prepared by passing nitric oxide into a solution of K_2SO_3 made alkaline with KOH. After recrystallizing the $K_2[(NO)_2SO_3]$ from hot water, a solution of it is reduced with sodium amalgam. The reactions are

$$2K^+ + SO_3^= + 2NO = K_2[(NO)_2SO_3]$$

and

$$(NO)_2SO_3^= + 6Na + 5H_2O = N_2H_4 + SO_4^= + 6Na^+ + 6OH^-$$

It is necessary to acidify the mixture after the reduction is complete, since the oxygen of the air slowly oxidizes the hydrazine to nitrogen and ammonia in alkaline solution.

From the hydrazine bisulfate obtained by the above methods of preparation, it is possible to prepare the monohydrate, $N_2H_4{\cdot}H_2O$ or N_2H_5OH, and anhydrous hydrazine itself, N_2H_4. The hydrate is prepared by distilling a mixture of KOH (100 g), water (250 g) and $N_2H_6SO_4$ (100 g) in a silver still. (The hydrate, like ammonium hydroxide, attacks glass slowly.) [Curtius and Schultz, *J. prakt. Chem.*, **123,** 1114 (1923).] Alternatively the hydrazine bisulfate can be converted to the bromide N_2H_5Br and this salt treated with KOH solution and alcohol; the KBr precipitates out, and the solution is subjected to distillation to remove the alcohol. The residue consists of a solution of hydrazine hydrate, and the hydrate is isolated by fractional distillation at 125 mm pressure [Lobry de Bruyn, *Rec. trav. chim.*, **18,** 297 (1899)].

Hydrazine hydrate, $N_2H_4{\cdot}H_2O$, is a colorless, fuming liquid (density = 1.0305 at 21°) which boils at 118.5° and at low temperatures solidifies to a colorless solid melting at −40°. Since the vapor, and doubtless the liquid also, dissociates reversibly into N_2H_4 and H_2O, it is not possible to say that the liquid is a pure substance. A mixture of 58.5% N_2H_4 and 41.5% H_2O has a higher boiling point than mixtures containing more or less hydrazine. The molecular weight from the vapor density of $N_2H_4{\cdot}H_2O$ at 98.8° and 366 mm is 31.6, and at 138° and 744.1 mm it is just one-half the formula weight. This shows that there is appreciable dissociation at 98.8° and 366 mm according to the equation

$$N_2H_4{\cdot}H_2O(g) = N_2H_4(g) + H_2O(g)$$

and at 138° and 744.1 mm the dissociation is effectively complete [Scott, *J. Chem. Soc.*, **85,** 913 (1904)]. The known vapor density data are not sufficient to permit of the calculation of thermodynamic quantities; since these calculations would be of interest, it is desirable to have careful measurements at more frequent temperature intervals, from, say, 90° to 130°. Such measurements might serve to throw more definite light on the nature of the bond between N_2H_4 and H_2O. Presumably the hydrate is $H_2N{-}NH_3OH$, since, as will be discussed below, in aqueous solution it has basic properties. The heats of formation of hydrazine hydrate and of anhydrous hydrazine are given in Table 27 [Hughes, Corruccini, and Gilbert, *J. Am. Chem. Soc.*, **61,** 2639 (1939)].

TABLE 27
THE HEATS OF FORMATION OF HYDRAZINE AND ITS HYDRATE

Compound	$\Delta H^{\circ}_{298.1}$ (cal/mole)
$N_2H_4(g)$	22,250
$N_2H_4(l)$	12,050
$N_2H_4H_2O(l)$	10,300
$N_2H_4(aq.)$	8,160

Hydrazine hydrate attacks cork, rubber, and, more slowly, glass. The bottles of the commercial product (concentrated aqueous solutions) frequently contain gelatinous precipitates of silica or silica hydrates. In the presence of air, slow oxidation to nitrogen, ammonia, and water takes place. Spontaneous decomposition into nitrogen, hydrogen, and ammonia appears to take place to some extent also; this decomposition is accelerated by the presence of spongy platinum [Tantar, *Z. phys. Chem.*, **40,** 475 (1904)].

Anhydrous hydrazine, N_2H_4, is prepared by dehydrating the hydrate with barium oxide, BaO. The dehydration with solid sodium hydroxide does not appear to be effective enough to obtain a pure product. In one method 100 cc of $N_2H_4 \cdot H_2O$ and 530 g of crushed BaO are heated together for one to three hours under a reflux condenser and in an atmosphere of nitrogen or hydrogen [Hale and Shetterly, *J. Am. Chem. Soc.*, **33,** 1071 (1911)]. The resulting liquid is fractionally distilled at low pressures (2–30 mm) in an atmosphere of hydrogen.

Another method for obtaining anhydrous hydrazine directly from the more common hydrazine bisulfate has been suggested by Browne and investigated by Friedrichs [*J. Am. Chem. Soc.*, **35,** 244 (1913)]. Advantage is taken of the reversibility of the reaction,

$$N_2H_6SO_4(s) + 2NH_3(l) = (NH_4)_2SO_4(s) + N_2H_4 \text{ [in } NH_3(l)]$$

and the process consists in the continuous extraction of only the hydrazine bisulfate with liquid ammonia at its boiling temperature, the ammonium sulfate being insoluble in this solvent [Franklin and Kraus, *Am. Chem. J.*, **20,** 820 (1898)]; the hydrazine is freed from ammonia by simple evaporation. This method appears adaptable to large-scale operations.

Anhydrous hydrazine is a colorless, fuming liquid which boils at 113.5°; at low temperatures it is a colorless solid melting at 1.8°. The liquid density is 1.0258 g/cc at 0° and 1.0114 g/cc at 15°. The vapor pressures are known, for the most part, only at and above the normal boiling point; these are 71 mm at 56°, 1.0 atm at 113.5°, 5 atm at 170° 56 atm at 300°, and 145 atm at 380°. The vapor has been shown to be monomeric [Giguère and Rundle, *J. Am. Chem. Soc.*, **63,** 1135 (1941)]. The critical temperature is 380°. These data give some indication of the relative inertness toward decomposition of anhydrous hydrazine, namely, that even at rather high temperatures it shows no tendency to decompose, although thermodynamically it is doubtless unstable with respect to decomposition into nitrogen, hydrogen, and ammonia, $2N_2H_4(g) = 2NH_3 + N_2 + H_2$. The dielectric constant of the liquid is 53 at 22°.

Anhydrous hydrazine burns in air and reacts violently with chlorine, bromine, and iodine. It also reacts in a lively fashion with $SOCl_2$ to yield $(H_2N_2H)_2SO$, a white solid, and N_2H_5Cl. With SO_2 the acid-like compound $HO_2SNHNHSO_2H$ results, of which two barium salts are known, namely, $Ba(O_2SNHNHSO_2)$ and $Ba_2(O_2SN_2SO_2)$. When vapors of SO_3 are allowed to react with anhydrous N_2H_4, a hydrazine sulfonic acid forms, $N_2H_3SO_3H$, and the latter with potassium nitrite yields KN_3SO_3 and water.

One of the remarkable properties of anhydrous hydrazine is its ability to dissolve sulfur. [See Ephraim and Piotrowsky, *Ber.*, **44,** 386 (1911), and adjoining articles These papers report several interesting reactions of N_2H_4.] The sulfur dissolves freely in the hydrazine (100 cc of N_2H_4 dissolves some 54 g of S at room temperature) to give a dark-red solution. The solutions are not completely stable, since a slow reaction, $3N_2H_4 + 2S = N_2 + 2N_2H_4H_2S$, takes place. The reaction decreases in rapidity with time, but after about twenty-four hours it is nearly complete; the color of the solution changes during the reaction period from dark red to a light yellow of low intensity. H_2S dissolves freely in N_2H_4 (l). Some ammonia is also formed in the sulfur solutions. These colored sulfur solutions may be used for the volumetric estimation of zinc or cadmium salts dissolved in hydrazine; ZnS and CdS are precipitated, and the disappearance of the color indicates the end point [Welsh and Broderson, *J. Am. Chem. Soc.*, **37,** 825 (1915)]. It must be presumed that the reactions involved are somewhat as follows:

$$N_2H_4 + S = S \text{ (in } N_2H_4) \tag{1}$$
$$3N_2H_4 + 2S = 2N_2H_4H_2S + N_2 \tag{2}$$
$$N_2H_4H_2S + CdI_2 = N_2H_4{\cdot}2HI + CdS \tag{3}$$

The rate of reaction (2) is apparently increased in some way as a result of reaction (3) taking place, since (2) is somewhat slow. Reaction (1) is doubtless not so simple as written, the true condition being probably represented by an equilibrium between hydrazine sulfide or polysulfide and a sulfur-nitrogen compound. In this connection, the solution of sulfur in liquid ammonia should be compared.

Iodine dissolves freely in hydrazine with vigorous or explosive reaction.

Metallic sodium reacts with anhydrous hydrazine at a moderate rate if the surface exposed is small, but it may react violently otherwise, to give a yellow solid or, with excess hydrazine, yellow solutions. The solid, NaN_2H_3, is soluble in hydrazine to give solutions that conduct electric current; the solid sometimes explodes violently. Sodium amide reacts with anhydrous hydrazine to form the same compound and ammonia. The reactions are [Welsh, *J. Am. Chem. Soc.*, **37,** 497 (1915)]

$$Na + N_2H_4 = NaN_2H_3 + \tfrac{1}{2}H_2$$
$$NaNH_2 + N_2H_4 = NaN_2H_3 + NH_3$$

The analogy between the group of compounds NaOH, $NaNH_2$, and NaN_2H_3 will be noted at once. The fact that one of the ammonia hydrogens has been replaced by $—NH_2$ in forming N_2H_4 does not completely inhibit the acid character of the remaining hydrogens.

From what has been said, anhydrous hydrazine has properties that recall those of liquid water, pure H_2O_2, and liquid ammonia. The acid constituent in the aqueous system is H^+ or H_3O^+, in the liquid ammonia system it is NH_4^+, and in the hydrazine system it would be $N_2H_5^+$. $N_2H_3^-$ would correspond to OH^-, and there is little doubt but that hydrazine solutions of N_2H_5Cl and NaN_2H_3 would, when mixed, react according to the equation

$$Na^+ + N_2H_3^- + N_2H_5^+ + Cl^- = Na^+ + Cl^- + 2N_2H_4$$

Because of the comparative difficulty of the experiments in the anhydrous hydrazine system, the detailed chemistry of neutralization, hydrazinolysis, and so on, has not been fully investigated. A few reactions of $N_2H_5^+$ in anhydrous hydrazine on metals have received attention; Cu, Sn, Al, and Zn are not appreciably attacked by such solutions. Magnesium and calcium, on the other hand, are readily attacked if $N_2H_5^+$ is present, but they suffer little or no dissolution in contact with anhydrous hydrazine alone. Accordingly, the reactivity of $N_2H_5^+$ in $N_2H_4(l)$ toward metals is much less than that of H_3O^+ in $H_2O(l)$ [see, for example, Welsh and Broderson, *J. Am. Chem. Soc.*, **37,** 825 (1915)].

Ammonia dissolves to a smaller extent in $N_2H_4(l)$ than in water. At 0° the three-phase system $N_2H_4(s)$, NH_3 [in $N_2H_4(l)$], $NH_3(g)$ shows a partial pressure of NH_3 of 175 mm, and the liquid phase consists of 98% N_2H_4 and 2% NH_3 by weight [Friedrichs, *Z. anorg. Chem.*, **127,** 221 (1923)]. At lower temperatures the solubility of ammonia is greater.

The high dielectric constant, 53, of anhydrous hydrazine suggests that it might prove to be an ionizing solvent for polar substances. Not only do solutions of salts in it conduct the electric current, but many salts are readily soluble in anhydrous hydrazine, as the following table shows [Welsh and Broderson, *J. Am. Chem. Soc.*, **37**, 816 (1915); Walden and Hilgert, *Z. phys. Chem.*, **A 165**, 241 (1933)].

Table 28
APPROXIMATE SOLUBILITIES OF SALTS IN ANHYDROUS HYDRAZINE AT ROOM TEMPERATURE
(S, in grams/100 cc N_2H_4)

Salt	S	Salt	S	Salt	S
NH_4Cl	75[a]	$MgSO_4$	0	Na_2CO_3	0
As_2O_3	1	$NiCl_2$	8	$NaNO_3$	26.6
H_3BO_3	55	KCl	8.5	Na_2SO_4	0
$CdBr_2$	40	KBr	56.4	$ZnCl_2$	8
$CaCl_2$	16	KI	135.7	RbCl	5
$CrCl_3$	13[b]	$NaClO_3$	66		
LiCl	16	NaCl	12.2		

[a] NH_3 is evolved.
[b] Red solution (complex), and some gas forms.

A number of other salts dissolve with reaction. Thus $AgNO_3$ is reduced to metallic silver; $NaBrO_3$ is reduced with the formation of a yellow solution. Precipitates of unknown composition result with $CuCl_2$ (brown), $PbCl_2$ and $Pb(NO_3)_2$ (yellow), $HgI_2(Hg)$, and $MgCl_2$ (white, flocculent). The nature of the precipitates is not exactly known; presumably in those cases where reduction is not evident, they consist of nitrides or hydrazinides, M_4N_2.

Aqueous solutions of hydrazine

The aqueous solutions of hydrazine or hydrazine hydrate are weakly alkaline. The reaction with water is, like that of ammonia,

$$N_2H_4 + H_2O = N_2H_5OH$$

and to indicate the basic property

$$N_2H_5OH = N_2H_5^+ + OH^-$$

$$\frac{(N_2H_5^+)(OH^-)}{(N_2H_5OH)} = 8.5 \times 10^{-7} \text{ at } 25^\circ$$

The ionization constant for ammonium hydroxide is 1.65×10^{-5}; that is, at the same total concentration, the (OH^-) in ammonium hydroxide solutions is about twenty times that in a hydrazinium hydroxide solution. The substitution of an $—NH_2$ for $—H$ in NH_3 decreases its basic character [Schwarzenbach, *Helv. Chem. Acta*, **19**, 178 (1936)].

Although $H_2N—NH_2$ is probably not a symmetric molecule, it is to be expected that the dihydroxide, $HOH_3N—NH_3OH$, would form and that the substance would be diacidic. In fact, it is possible to prepare the dichloride, $N_2H_6Cl_2$, and the corresponding nitrate and sulfate by the addition of excess acid and subsequent recrystallization. The second OH^-, however, ionizes much less freely than does the first,

$$\frac{(N_2H_6^{++})(OH^-)}{(N_2H_6OH^+)} = 8.9 \times 10^{-16} \text{ at } 25°$$

and, accordingly, aqueous solutions of $N_2H_6Cl_2$ or similar salts will show extensive hydrolysis and the solutions will be acid. When solutions of N_2H_4 in water are titrated electrometrically with strong acids, only one inflection point is observed, which is to be expected if the second ionization constant of $N_2H_6(OH)_2$ is as small as the value just given [Gilbert, *J. Am. Chem. Soc.*, **46**, 2648 (1924)]. The titration of hydrazine sulfate solutions, $N_2H_6SO_4$, with strong bases yields two inflection points, the first corresponding to the neutralization of the acid in $N_2H_5^+ + H^+ + SO_4^=$ and the second to the conversion of $N_2H_5^+$ to N_2H_5OH.

The important salts of hydrazine are the chloride, N_2H_5Cl, the nitrate, $N_2H_5NO_3$, and the bisulfate, $N_2H_5HSO_4$, of which the last is by far the most common and most readily prepared. The chloride is very soluble in water; it melts at 89° and decomposes at higher temperatures. The dichloride is more soluble than the chloride; it may be obtained as octahedral crystals. Hydrazine nitrate is also very soluble in water, 76.61 g being contained in 100 g of the saturated solution at 25°, but it is sparingly soluble in alcohol; it melts at 70.7° and decomposes fairly rapidly at 200°. The bisulfate, $N_2H_5HSO_4$, is much less soluble in water than the other inorganic salts; the solubility is depressed by the presence of sulfate ion, as the mass law would predict [Sommer and Weise, *Z. anorg. Chem.*, **94**, 51 (1916)].

Table 29
SOLUBILITY OF HYDRAZINE BISULFATE IN WATER
(S expressed in g/100 g water.)

t(°C)	S
20	2.861
25	3.415
40	5.249
60	9.077
80	14 39

The normal sulfate, $(N_2H_5)_2SO_4$, is much more soluble than the bisulfate; 100 g of water dissolves 202.2 g at 25°.

Hydrazine in aqueous solutions shows itself to be both an oxidizing and a reducing agent. With such reducing agents as Zn, Sn, Sn^{++}, and Ti^{+++} reduction to ammonia is observed, while with oxidizing agents the product is most frequently nitrogen, although in some cases ammonia and hydrazoic acid, HN_3, are also formed. In agreement with the asserted similarity of hydrazine to hydrogen peroxide, the oxidation to nitrogen is to be expected; thus

$$H_2O_2 + \text{Oxidizer} = 2H^+ + O_2 + \text{Reduced form of oxidizer}$$
$$N_2H_5^+ + \text{Oxidizer} = 5H^+ + N_2 + \text{Reduced form of oxidizer}$$

The oxidation reactions have been carefully studied by Bray and Cuy [*J. Am. Chem. Soc.*, **46,** 1796 (1924), *et ante*].

The reaction of $N_2H_5^+$ with chlorine or bromine proceeds rapidly and quantitatively in acid solutions.

$$N_2H_5^+ + 2Br_2 = N_2 + 5H^+ + 4Br^-$$

Hypochlorous acid in a buffer solution of NaH_2PO_4—Na_2HPO_4 (to prevent the decomposition of HClO into H_2O and Cl_2 and thus loss by volatilization) also rapidly oxidizes hydrazinium salts quantitatively to nitrogen. Pentavalent vanadium in acid solution, VO_2^+, rapidly oxidizes $N_2H_5^+$ principally to nitrogen, but the reaction is not quite quantitative, an error of $\frac{1}{2}\%$ or more being possible. With dichromate in acid solution, nitrogen is the principal product; but some NH_4^+ and HN_3 are also observed; the dichromate reaction proceeds with a measurable rate which is first-order with respect to both dichromate and hydrazinium ions [Seubert and Carstens, *Z. anorg. Chem.*, **56,** 357 (1908)]. Ferricyanide ion reacts rapidly in alkaline solution with $N_2H_5^+$ to give nitrogen and ferrocyanide, but in acid solution the reaction is slow. In 0.3 n to 2 n acid solution iodate oxidizes $N_2H_5^+$ rapidly and quantitatively to nitrogen, but in alkaline solution the reaction is slow. The reaction with iodine is slow in acid but rapid in alkaline solution, a fact that is probably to be related to the concentration of hypoiodite, this being largest in alkaline solution. Unlike the cases just described, the oxidation of $N_2H_5^+$ by permanganate in acid solution, although rapid, is far from quantitative, the number of oxidation equivalents of permanganate required per mole of $N_2H_5^+$ varying from 1.4 to 1.7. This number would be 4.0 if only nitrogen were the oxidation product; in alkaline solution 3.9 equivalents are observed, and this suggests that in acid solution some intermediate oxidation state of manganese affects the course of the reaction. The observations of Cuy, Rosenberg, and Bray showed that manganic salts, Mn^{+++}, oxidize $N_2H_5^+$ mainly according to the equation

$$Mn^{+++} + N_2H_5^+ = NH_4^+ + \frac{1}{2}N_2 + Mn^{++} + H^+$$

in acetic acid solution. If the direct reaction with permanganate is

$$4MnO_4^- + 5N_2H_5^+ + 7H^+ = 5N_2 + 4Mn^{++} + 16H_2O$$

and if for every mole of MnO_4^- reacting in this way one mole reacts with Mn^{++} to form Mn^{+++}, and if this in turn oxidizes hydrazine as indicated, then 1.6 equivalents of MnO_4^- per mole of hydrazine would be required. This conclusion is in fair agreement with the number of equivalents observed; namely, 1.4–1.7. In this case the net reaction would be

$$8MnO_4^- + 25N_2H_5^+ + 19H^+ = 20NH_4^+ + 15N_2 + 32H_2O + 8Mn^{++}$$

Hydrazinium salts act as reducing agents toward many other oxidizing agents, the products being principally nitrogen together with some ammonia and hydrazoic acid in a few cases. Ammoniacal silver solutions give silver mirrors, and Fehling's solution ($CuSO_4$ + KOH + tartrate) is reduced to cuprous oxide. Of special interest is the effect of oxygen on alkaline solutions of N_2H_5OH. It was once supposed that spontaneous decomposition of the hydrazinium hydroxide into nitrogen and ammonia took place, but more careful observations show that in the absence of oxygen the solutions do not change in strength. With oxygen of the air, a 0.05 m solution of N_2H_5OH in 0.5 n OH^- may be oxidized to the extent of 1% in five minutes and 20% in 16 hours. A neutral, 0.015 m N_2H_5OH solution loses, by atmospheric oxidation, about 8% of its strength in 48 hours.

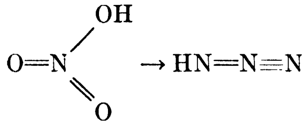
Of interest is the catalyzed reaction of $N_2H_5^+$ with chlorate in acid solution. With chlorate alone, the reaction is extremely slow, if it takes place at all. On the addition of a small amount of osmium salt, the evolution of nitrogen sets in slowly at first and then proceeds more rapidly until one of the reactants is used up. The mechanism of the reaction is not known; some unpublished results indicate that osmium acts by being oxidized to OsO_4 by chlorate, the tetroxide then reacting with the hydrazine. That this is not the complete explanation is indicated by the autocatalytic nature of the reaction.

We may conclude our discussion of hydrazine by calling attention once more to its twofold character. First, it acts as both a reducing and an oxidizing agent; second, its structure, because it is a derivative of ammonia, is such that its physical and chemical properties are intermediate between those of ammonia and its analogue, water. Efforts to prepare further derivatives such as $NH(NH_2)_2$ and $N(NH_2)_3$ do not appear to have been successful. (Judging from the properties of NH_3 and N_2H_4, $NH(NH_2)_2$ would be a liquid of high dielectric constant.)

The geometrical structure of hydrazine has not been established; it would be of interest to know whether or not the $—NH_2$ groups rotate freely about the nitrogen—nitrogen bond. Electron-diffraction experiments show the N—N distance to be 1.47 Å, but the bond angles, H—N—N, are not known [Schomaker and Giguère, unpublished results]. According to our current ideas, the two nitrogens are bonded together through an electron pair; and since the hydrogens are bound to the nitrogens in the same manner, each nitrogen would have a valence of three.

Hydrazoic Acid, HN_3

So far we have discussed a number of compounds which were regarded as derivatives of ammonia, but when we consider hydrazoic acid, HN_3, it soon becomes apparent that it cannot be so derived directly from ammonia alone. Franklin, who has given much attention to this compound, chooses to regard it as an ammono nitric acid, although he properly points out that the chemical evidence has not been sufficient to establish its structure [Franklin, *Nitrogen System of Compounds*, Reinhold, New York, 1935, Chap. XIV]. Thus, if we proceed formally, we see that



$$\mathrm{O{=}N(OH){=}O} \rightarrow \mathrm{HN{=}N{\equiv}N}$$

Nitric Acid **Hydrazoic Acid**

where one =O is replaced by =NH, and —OH and the remaining =O are together replaced by ≡N. The structure presented implies that one of the nitrogens differs from the other two, and, moreover, that one nitrogen is bound by a triple bond and the other by a double bond to the central nitrogen. From this one would predict the two N-to-N distances to be different. X-ray and electron-diffraction studies [Hendricks and Pauling, *J. Am. Chem. Soc.*, **47,** 2904 (1925); Brockway and Pauling, *Proc. Nat. Acad. Sci.*, **19,** 860 (1933)] show both distances to be the same in crystals of NaN_3 and KN_3, while in CH_3N_3 the azide group is unsymmetrical, namely, $H_3C{-}N{=}N{\equiv}N$. More recently Eyster [*J. Chem. Phys.*, **8,** 135 (1940)] has analyzed the fine structure of the infrared absorption bands for $HN_3(g)$ and finds that the results are in accord with the structure shown in Fig. 20. In the alkali azides, methyl azide, and HN_3, the nitrogens are colinear; there appears no good reason for believing that ring or cyclic structures are possible. The resonating electronic structure now accepted is

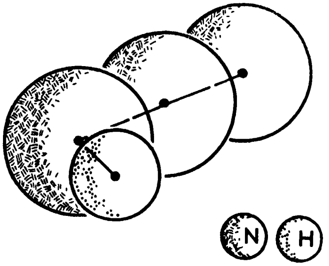
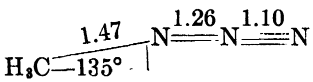


Fig. 20. The Molecular Structure of HN_3. $H{-}N = 1.012$Å; $N_1{-}N_2 = 1.241$Å; $N_2{-}N_3 = 1.128$Å; $\angle H{-}N_1{-}N_2 = 110°\,52'$.

$$\mathrm{H}:\overset{..}{\mathrm{N}}::\overset{+}{\mathrm{N}}::\overset{\overset{-}{..}}{\mathrm{N}}:,\qquad \mathrm{H}:\underset{..}{\overset{..}{\mathrm{N}}}:\overset{-}{\mathrm{N}}:::\overset{+}{\mathrm{N}}:$$

the form on the right predominating. The space structure of CH_3N_3, as derived from the results of electron-diffraction experiments, is



$$\mathrm{H_3C}\overset{1.47}{\text{—}}\mathrm{N}\overset{1.26}{=}\mathrm{N}\overset{1.10}{\equiv}\mathrm{N},\quad \angle 135°$$

where the distances are expressed in Ångstrom units. In crystals of th alkali azides, the azide ion has the linear structure $:\ddot{N}::N::\ddot{N}:^{-}$, with the N═N distances 1.16 Å.

There is little point in trying to force the ammonia-water analogies too far in an attempt to describe the properties of compounds. Hydrazoic acid has also been considered a hydrazine derivative of nitrous acid, HNO_2, in that the —OH and ═O groups are regarded as replaced by one $\equiv N_2H$ group. Still another view (Browne) is that HN_3 is an ammonia derivative of hyponitrous acid, $H_2N_2O_2$, the two —OH groups being replaced by an ═NH group. These two pictures, together with that presented above, have been of some assistance in explaining or predicting some reactions, but it is doubtful whether they are of any fundamental significance. Indeed, as is often the case, analogies and forced pictures may do harm in that their adoption can close the way to a deeper insight into the problem.

The preparation of hydrazoic acid can be effected in a variety of ways, of which only the most important will be discussed here.

(1) $3NaNH_2(l) + NaNO_3 = NaN_3 + 3NaOH + NH_3$. In this method, powdered sodium nitrate is added cautiously and slowly to pure, molten sodium amide at 175°. The reaction is a vigorous one, and yields as high as 65%, based on the nitrate, are obtainable [Browne and Wilcoxon, *J. Am. Chem. Soc.*, **48**, 682 (1926)]. Nitrogen and hydrogen are also formed, but no oxygen or oxides or nitrogen. A variant of this method, and the one first discovered, is that of Franklin [*J. Am. Chem. Soc.*, **56**, 568 (1934); *Science*, **56**, 28 (1922)], which consists in heating liquid ammonia solutions of potassium amide and nitrate in a metal bomb to 120–140°; the yield can be as high as 75%. The yields with the sodium salts are lower, 16%, but solutions of lead nitrate and excess potassium amide in liquid ammonia lead to 80% yields of $Pb(N_3)_2$. Iron salts inhibit the reaction, and the yield becomes zero if tubes of ordinary steel are used as vessels. The alkali amide is necessary for reaction; solutions of alkali or ammonium nitrates alone in liquid ammonia do not yield azides when heated. Efforts to bring about the reverse of the main reaction have not been successful.

(2) $2NaNH_2(l) + N_2O(g) = NaN_3(s) + NaOH(s) + NH_3(g)$. Nitrous oxide is passed over molten sodium amide at 190° ± 4° in a nickel vessel. Yields as high as 90%, based on the reaction as written, are obtainable; the method is employed in the commercial preparation of sodium azide. After the reaction is complete, the resulting mixture is dissolved in water, and the NaN_3 is then recrystallized from the solution. The reaction was discovered by Wislicenus (1892) and later investigated more thoroughly by Dennis and Browne [*J. Am. Chem. Soc.*, **26**, 577 (1904)]. It will be noted that

only one-half of the amide nitrogen is available for the formation of sodium azide; the ammonia that is formed in the reaction can, of course, be used to prepare sodium amide by causing it to react with metallic sodium.

$$Na + NH_3 = NaNH_2 + \tfrac{1}{2}H_2$$

(3) $N_2H_5^+ + HNO_2 = HN_3 + H^+ + 2H_2O$. This was the reaction employed by Curtius, the discoverer of hydrazoic acid, for the preparation of the compound [*Ber.*, **26,** 1263 (1892)]. The best conditions for high yields were investigated by Sommer and Pincas [*Ber.*, **49,** 259 (1916)], who found that the acidity of the solutions played an important role. At high acid concentrations, nitrous acid rapidly oxidizes the hydrazoic acid formed; if the acidity is too low, a reaction forming N_2O becomes important. Sommer and Pincas found that a mixture made from 400 cc of 16.5–25% H_3PO_4, 27.6g N_2H_5Cl, and 1.35g $NaNO_2$ in 400 cc water gave a yield of 59.6% based on the nitrite used. The nitrite solution is added slowly and with constant stirring to the hydrazine-phosphoric acid mixture at room temperature.

(4) $N_2H_5^+$ + Oxidizing Agents = HN_3. Browne and Shetterly [*J. Am. Chem. Soc.*, **31,** 221 (1909), *et ante*] studied the effect of a variety of oxidizing agents on hydrazine sulfate solutions with respect to the quantity of hydrazoic acid formed. The oxidizing agent in aqueous solution is usually added to a heated (80°) solution of hydrazine sulfate. The following table summarizes their most

TABLE 30
THE OXIDATION OF HYDRAZINE TO HYDRAZOIC ACID AT 80°

Volume and Concentration of Hydrazine Sulfate Solution	Oxidizing Agent	Per Cent Yield of HN_3 or NaN_3
5 g in 500 cc 6 n H_2SO_4	H_2O_2 (100 cc 1 m)	28
100 cc (10 g/l)	H_2O_2 (alkaline soln.)	0.0
30 cc (10 g/l)	NH_4VO_3 (1 g in 120 cc) 6 n H_2SO_4	13.6
30 cc (10 g/l)	$KClO_3$ (in 6 n H_2SO_4)	20
30 cc (10 g/l)	$KBrO_3$ (in H_2SO_4)	6.7
100 cc (10 g/l)	$K_2S_2O_8$ (4.2 g in 50 cc conc. H_2SO_4)	40
100 cc (10 g/l)	$K_2S_2O_8$ (in alkaline soln.)	1
100 cc (10 g/l)	$KMnO_4$ (in acid soln.)	3
100 cc (10 g/l)	$KMnO_4$ (in alkaline soln.)	0.0
100 cc (10 g/l) (reactants mixed and boiled)	$KClO_4$ (14 g + 5 cc conc. H_2SO_4)	22
100 cc (10 g/l) (reactants mixed and boiled)	PbO_2 and MnO_2 (in H_2SO_4)	4 or less

important results. The effect of acid is often marked; when specified, the acid concentrations given in the table are for optimum yields. Not enough is known about the detailed mechanisms of these reactions to permit any relevant remarks on the effect of acid concentration.

(5) $N_2H_5OH + NCl_3 + 4OH^- = N_3^- + 3Cl^- + 5H_2O$. In this method a solution of NCl_3 in benzene is shaken with an alkaline solution of hydrazine sulfate. Under such conditions yields of 36%, based on NCl_3, are obtained; but if the aqueous layer becomes acid, the yield is low [Tantar, *Ber.*, **32**, 1399 (1899)].

The above list of the important reactions in which hydrazoic acid or its salts are formed does not include a number in which moderate yields are obtainable. For example, the oxidation of solid hydrazine bisulfate with warm, 10 n nitric acid leads to a 10% yield of HN_3. Also if benzoyl-hydrazine is treated with nitrous acid, and if the resulting benzoyl azide is then hydrolyzed with sodium ethylate, fair yields of HN_3 result. These methods do not appear to be different in principle from (3); it is conceivable that the first step in the nitric acid method consists in the reduction of HNO_3 to nitrous acid, and the subsequent steps would be much the same as those involved in (3). It would be of interest and value to study the rate of one or more of the aqueous solution reactions and from the results arrive at a mechanism of the reaction. An investigation of one or two clear-cut cases might well throw considerable light on the nature and steps of the reactions leading to the formation of hydrazoic acid.

Free hydrazoic acid, HN_3, is readily obtainable from its acidified solutions by distillation. For this purpose moderately strong sulfuric acid is usually used. Anhydrous HN_3 is most conveniently prepared by allowing strong sulfuric acid to drop slowly on solid potassium or sodium azide. Gaseous HN_3 may be dried with anhydrous calcium chloride and then condensed to a colorless mobile liquid which is fearfully and

TABLE 31

VAPOR PRESSURES AND DENSITY OF HYDROGEN AZIDE

t (°C)	Vapor Pressure (mm Hg)	t (°C)	Vapor Pressure (mm Hg)
−78.0	2.3	0.0	163.7
−40.0	28	15.0	321
−23.0	55	24.7	509
−18.0	64		

$$\text{Liquid: } d^t_{4^\circ} = \frac{1.126}{1 + 0.0013t} \qquad (0^\circ < t < 21^\circ)$$

dangerously explosive. The liquid is readily detonated by sharp blows, and even when boiling, in the presence of fragments of glass or alone, it may explode. The explosions have a very high intensity over a small (60 cm) radius. During experimentation with the liquid, it should be kept behind a thick piece of safety glass. The vapors are poisonous, and care should be taken to avoid inhaling them.

As a consequence of the explosive property of liquid HN_3, its physical constants have not been carefully determined. It boils at 37°, and when it is cooled to low temperatures, a colorless solid forms which melts at −80°. The vapor pressures and density have been determined by Günther, Meyer, and Müller-Skjold [*Z. phys. Chem.*, **A 175**, 154 (1935)].

The vapor density at both low and ordinary pressures corresponds to the monomer HN_3 [Beckman and Dickinson, *J. Am. Chem. Soc.*, **50**, 1870 (1928)]. Gaseous hydrogen azide is colorless and does not absorb light in the visible region, but it does absorb in the ultraviolet (2400 Å and shorter wave lengths) with decomposition. When heated, the vapor begins to decompose at a measurable rate at 290°. There is little pressure increase in the thermal decomposition; the products consist of N_2, H_2, and NH_3, and on cooling a white solid, ammonium azide, NH_4N_3, deposits on the vessel walls. The thermal decomposition is strongly influenced by the nature of the walls of the vessel [Ramsperger, *J. Am. Chem. Soc.*, **51**, 2134 (1929)].

The dielectric constant of liquid hydrogen azide is not known, but that it is appreciable is indicated by the fact that the liquid dissolves several salts, and the resulting solutions are conductors of electricity [see Audrieth, *Chem. Rev.*, **15**, 169 (1934) for an excellent review of hydrazoic acid and a report on the unpublished solubility experiments of McKinney]. At 0° NH_4Br, NH_4I, $CoCl_2$, $MgCl_2$, KCl, KBr, KI, KN_3, NaBr, NaI, and $HgCl_2$ are appreciably soluble in $HN_3(l)$. Nitrates, sulfates, oxides, carbonates, and sulfides are in general not appreciably soluble. Iodine dissolves readily in the liquid to give a reddish solution which conducts electric current; this fact may be due to the reaction $HN_3(l) + I_2 = H^+ + I^- + IN_3$, iodine azide being a known compound. The free energy of formation of gaseous hydrogen azide is $\Delta F^\circ_{298.1} = 78{,}525$ cal/mole [Eyster and Gillette, *J. Chem. Phys.*, **8**, 369 (1940)]. The result is based upon calculations from molecular constants and the value of $\Delta E = 70{,}900$ cal/mole [Günther, Meyer, and Müller-Skold, *Z. phys. Chem.*, **A 175**, 154 (1935)]. The molal entropy of the ideal vapor at 1 atm and 298.1°K is 56.74 cal/deg.

Hydrazoic acid is a weak acid. The ionization constant at 25° [West, *J. Chem. Soc.*, **77**, 705 (1900)] is

$$\frac{(H^+)(N_3^-)}{(HN_3)} = 1.8 \times 10^{-5}$$

and this value is substantially equal to that for acetic acid. The salts of hydrazoic acid resemble in many ways the halide salts. Indeed, the azide group shows many reactions and properties that recall those of the halides and haloids, F^-, Cl^-, Br^-, I^-, CNS^-, CNO^-, and CN^-. Thus AgN_3 and HgN_3 are insoluble in water at room temperatures, and with Fe^{+++} a highly red-colored, weak electrolyte $Fe(N_3)_3$ is formed on the addition of N_3^-.

The normal azide salts of Pb, $Hg^{I,II}$, Tl, and Ba explode on being struck sharply, and they have found application as detonators; the decomposition products are nitrogen and either the metal or a simple nitride of it. The alkali metal azides have the interesting and important property of decomposing into nitrogen and the metal when heated to about 300° or higher [Tiede, *Ber.*, **49,** 1742 (1916); Suhrman and Clusius, *Z. anorg. Chem.*, **152,** 52 (1926); Mott, *Proc. Roy. Soc.*, **172A,** 325 (1939)], and once decomposition starts, it will continue at somewhat lower temperatures. The decomposition reaction of NaN_3 in the absence of air or moisture is

$$NaN_3\,(s) = Na\,(l) + \tfrac{3}{2}N_2\,(g)$$

and it goes to completion with no side reactions, so that a 100% yield of sodium metal and nitrogen is attainable. The other alkali metals form small amounts of nitrides, and the yield of metal and nitrogen is not 100%. Advantage may be taken of the reaction for the preparation of the alkali metals or of very pure nitrogen.

TABLE 32
PROPERTIES OF ALKALI METAL AZIDES

Azide	Yield of Metal on Heating (%)	Temperature of Decomposition (°C)	Solubility in 100 g Water at 17° (g)
LiN_3	—	—	66.41
NaN_3	100	300	41.7 (16°)
KN_3	80	320	49.6
RbN_3	60	310	114.1
CsN_3	90	350	307.4 (16°)

The thermal decomposition of the alkaline earth and heavy metal azides also leads to nitrogen and the metal or metal nitride. The nitrogen obtained is especially pure and may be used for spectroscopic or atomic-weight purposes.

In general, solutions of the azides are not very reactive to oxidizing and reducing agents at room temperature. On heating with hydrochloric, hydrobromic, or hydriodic acid, the free halogen is liberated, but not in a clean-cut manner. Many metals, even the noble ones, are slowly oxidized by hydrazoic acid, with the formation of the azides, ammonium salts, nitrogen, and variable quantities of hydrazine. Titanous and chromous ions reduce HN_3 solutions readily to nitrogen and ammonia in acid solution, one mole of ammonia being formed per mole of hydrazoic acid reduced [Piccard and Thomas, *Helv. Chim. Acta*, **6,** 1039 (1923)]. Stannous chloride and sulfurous acid also reduce hydrazoic acid to ammonia and nitrogen. It has been assumed that an intermediate substance, triazene, H_3N_3, is the first reduction product of HN_3, although this compound has never been isolated; the triazene is then assumed to decompose into other intermediates or into ammonia and nitrogen directly. The evidence for these intermediates is mostly indirect [see Audrieth, *Z. phys. Chem.*, **165,** 323 (1933)].

Aqueous hydrazoic acid ordinarily reacts slowly with oxidizing agents at room temperature. Ferric salts, iodic acid, and hydrogen peroxide do not show appreciable oxidizing action. Bromate in acid solution reacts at a measurable rate to give gaseous products whose composition is not known. Chloric acid and manganese dioxide react only slowly if at all at ordinary temperatures. Permanganate in acid solution oxidizes hydrazoic acid fairly rapidly, but the products are variable in amount and consist mainly of N_2, HNO_3, and oxygen; the resulting mixtures have a slow oxidizing action on iodide which has led to the doubtful supposition that oxyacids of the form HN_3O and HN_3O_3, the analogues of HClO and $HClO_3$, are present. Permanganate cannot be used as a reagent for the volumetric estimation of the azides, since the reactions are complex and the products are variable [Raschig, *Schwefel und Stickstoffstudien*, Verlag Chemie, Leipzig, 1924]. Hypochlorous and nitrous acids and ceric salts bring about the complete and rapid oxidation of HN_3 according to the reactions

$$\begin{aligned} HClO + HN_3 &= ClN_3 + H_2O \\ HN_3 + ClN_3 &= H^+ + Cl^- + 3N_2 \\ HNO_2 + HN_3 &= N_2 + N_2O + H_2O \\ 2Ce^{++++} + 2HN_3 &= 2Ce^{+++} + 3N_2 + 2H^+ \end{aligned}$$

The two latter oxidizing agents may be used for the quantitative estimation of azides, the ceric salts being somewhat the better for the purpose [Sommer and Pincas, *Ber.*, **48,** 1963 (1915)]. When a gravimetric method is called for, it is common practice to precipitate silver azide and convert the filtered precipitate to the nitrate and then to the chloride; AgN_3 itself may be dried at 100° and weighed as such, although it is explosive when struck.

Hydrazoic acid and iodine react only in the presence of a catalyst, and the known catalysts are thiosulfate, carbon disulfide, and azidodithiocarbonic acid, $HSCSN_3$. The latter compound is formed by the interaction of solutions of hydrazoic acid or its salts with carbon disulfide [Currier and Browne, *J. Am. Chem. Soc.*, **44,** 2849 (1922)]. When definite volumes of standard solutions of iodine or I_3^- and HN_3 are mixed, no reaction is observed, but if titration of the iodine in the mixture with thiosulfate is begun, an evolution of gas, nitrogen, is observed, and the thiosulfate required is less than that corresponding to the initial iodine added. The difference between the observed and calculated quantities of thiosulfate may be nearly zero if the HN_3 solution contains an added strong acid, and it is greatest when the acid concentration corresponds to that in an equimolal Na_2HPO_4—NaH_2PO_4 buffer solution. The addition, before titration is begun, of tetrathionate has no appreciable effect. These facts suggest that the intermediate responsible for the oxidation of the azide is a complex between iodine and thiosulfate, $(I_2S_2O_3)^=$, and that N_3^- is more reactive to the complex than is un-ionized HN_3. It appears that the rate of the reaction between N_3^- and $(I_2S_2O_3)^=$ is more rapid than that between the complex and $S_2O_3^=$ to form $S_4O_6^=$ $+ 2I^-$. If the initial iodine is in considerable excess and if the solution is properly buffered, the catalyzed oxidation can be nearly quantitative according to the reaction,

$$2N_3^- + I_2 = 2I^- + 3N_2$$

Attention has already been called to the similarity between the azides and halides, and this similarity suggests that azide compounds similar to ICl, ICN, and other interhalogen compounds might exist. The colorless gas chlorine azide, ClN_3, results when an aqueous mixture of sodium hypochlorite and azide is acidified with acetic or boric acid [Raschig, *Ber.*, **41**, 4194 (1908); Glen, *Z. physik.*, **38**, 176 (1926)]; the compound is highly and dangerously explosive. Bromine azide, BrN_3, is prepared by treating silver or sodium azide with a solution of bromine in ether or benzene, or by letting bromine react with dry sodium azide. BrN_3 is a mobile, volatile, orange-red liquid which freezes to a red solid at about −45° [Spencer, *J. Chem. Soc.*, **127**, 217 (1925)]. With water, hydrolysis sets in and the resulting hydrazoic acid is oxidized to nitrogen. BrN_3 is probably explosive. Iodine azide, IN_3, is an unstable, light-yellow solid which is formed when an aqueous suspension of AgN_3 is treated with an ether or benzene solution of iodine. IN_3 is somewhat soluble in water and is hydrolyzed by alkali [Hantzsch, *Ber.*, **33**, 522 (1900); Gutman, *Ber.*, **57**, 1956 (1924)].

Cyanogen azide, CNN_3, is a solid melting at 40.3° to a liquid which explodes at 170°, and is obtained from the reaction between BrCN and NaN_3 [Hart, *J. Am. Chem. Soc.*, **50**, 1922 (1928)]. It is soluble in alcohol, ether, and chloroform; with ether solutions of ammonia it reacts to give $NCN(NH_2)N_3$, and with water it hydrolyzes to CO_2, HN_3, and $CNNH_2$. Cyanuric azide, $(CNN_3)_3$, is formed by the action of $(CNCl)_3$ on NaN_3, or through reactions involving organic hydrazides; it may find application as a detonator [Taylor and Rinkenback, *J. Franklin*

Inst., **204,** 369 (1927)]. When warmed with aqueous sodium hydroxide, $(CNN_3)_3$ hydrolyzes quantitatively to $Na_3C_3O_3N_3$ and NaN_3; with an ether solution of ammonia, one azide group is replaced by an $-NH_2$ group to give $CNNH_2(CNN_3)_2$ [see Franklin, *The Nitrogen System of Compounds*].

A number of other azides, the analogues of the corresponding chlorides, are known, among which are $SO(N_3)_2$ (from $SOCl_2 + 2NaN_3$), a colorless, explosive liquid, KSO_3N_3 (from $NH_2NHSO_3H(s) + KNO_2$ (conc. soln.)), a colorless explosive solid and the analogue of chlorosulfonic acid, HSO_3Cl, and $CO(N_3)_2$, an explosive solid which may be regarded as the analogue of phosgene, $COCl_2$, although it does not appear to have been prepared directly from this substance. The compounds cited leave no doubt about the general nature of the azide group and its similarity to the halogens and the haloids.

CHAPTER 4

Ammonia and Liquid Ammonia Solutions

Ammonia, NH_3, is the most stable and important of the hydrogen compounds of nitrogen. At room temperature it is a colorless gas with a distinctive odor; at lower temperatures it condenses, first to a colorless liquid boiling at $-33.4°$ and then to a colorless solid melting at $-77.74°$. Large quantities of ammonia are produced at one stage or another in several important industrial processes for the fixation of nitrogen (see Chapter 1). An especially pure product is obtained in the Haber process for the direct combination of nitrogen and hydrogen, and most commercial ammonia sold as such is made in this way. The most convenient laboratory method for the preparation of pure ammonia is to treat ammonium chloride with a saturated potassium hydroxide solution. The resulting gas is dried with solid potassium hydroxide and then with sodium. A final distillation with proper precautions yields an ammonia with only about 0.001 mole per cent impurity [Overstreet and Giauque, *J. Am. Chem. Soc.*, **59**, 254 (1937)].

Physical properties of ammonia

The ammonia molecule has the form of a low pyramid of height 0.360 Å. This configuration gives rise to the possibility of the nitrogen atom passing from its equilibrium position on one side of the plane of the hydrogen atoms through the plane to an equally stable position on the other side. The theoretical problem presented by an atom or group of atoms having two equally stable equilibrium positions (the double minima problem) is of great interest and has been solved in considerable detail for the simple case of ammonia [Hund, *Z. Physik*, **43**, 805 (1927); Dennison and Uhlenbeck, *Phys. Rev.*, **41**, 313 (1932); Manning, *J. Chem. Phys.*, **3**, 136 (1935)]. The double minima problem occurs in complicated molecules also, and its correct treatment is of importance in the calculation of thermodynamic functions. [There is an excellent discussion by Pitzer, *J. Chem. Phys.*, **7**, 251 (1939).] The experimental evidence that the nitrogen atom in ammonia has double minima may be regarded as conclusive, as all available spectroscopic data are explained quantitatively [Wu, *Vibrational Spectra and Structure of Polyatomic Molecules*, p. 191, National Univ. of Peking, Kun-ming, China, 1939]. Deuteroammonia, ND_3, has the same interatomic distances as NH_3 and its spectrum has aided in solving the ammonia problem. The constants for the molecules are given below [Wright and Randall, *Phys. Rev.*, **44,** 391 (1933); Migeotte and Barker, *Phys. Rev.*, **50,** 418 (1936); dipole moment, de Bruyne and Smythe, *J. Am. Chem. Soc.*, **57,** 1203 (1935)].

	NH_3	ND_3
Moment of inertia:		
A_0	2.782×10^{-40} gcm²	5.397×10^{-40} gcm²
C_0	4.497×10^{-40}	8.985×10^{-40}
Height of molecule	0.360 Å	0.360 Å
N—H or N—D	1.016	1.016
H—H or D—D	1.645	1.645
Fundamental vibrations:		
$\omega_1 \parallel$*	3337 cm^{-1}	2420 cm^{-1}
$\omega_2 \perp$	3415	2556
$\omega_3 \parallel$	933, 967	745.8, 749.2
$\omega_4 \perp$	1628	1191.3
Dipole moment	$1.46_6 \times 10^{-18}$ e.s.u.	$1.49_6 \times 10^{-18}$ e.s.u.

* The parallel vibrations are double because of the double minima, but the splitting of ω_1 is very small.

The macroscopic physical properties of ammonia have also been extensively investigated, owing partly to the widespread use of the chemical in refrigeration systems. Very accurate values have been determined by the United States Bureau of Standards for the vapor pressure [Cragoe, Meyers, and Taylor, *J. Am. Chem. Soc.*, **42,** 206 (1920)], the heat of vaporization [Osborne and Van Dusen, *J. Am. Chem. Soc.*, **40,** 14 (1918)], and the density [Cragoe and Harper, *Bur. Stand. Sc. Pp.*, **420,** 313 (1921)] from −80° to +70°C. The thermodynamic properties of ammonia are summarized in Table 33 [Overstreet and Giauque, *J. Am. Chem. Soc.*, **59,** 254 (1937); spectroscopic entropy, Stephenson and McMahon, *ibid.*, **61,** 437 (1939); dielectric constant, Grubb, Chittum, and Hunt, *ibid.*, **58,** 776 (1936); viscosity, Plank and Hunt, *ibid.*, **61,** 3590 (1939)]. It is surprising that the boiling point is not more accurately known; the best values are −33.35° [Cragoe, Meyers, and Taylor, *J. Am. Chem. Soc.*, **42,** 206 (1920)], −33.34° [Henning and Stock, *Z. Physik*, **4,** 226 (1921)], and −33.42° [Overstreet and Giauque, *loc. cit.*].

TABLE 33

THE PHYSICAL AND THERMODYNAMIC PROPERTIES OF AMMONIA

(0°C = 273.1°K)

Melting point	195.36°K	ΔH (fusion)	1352 cal/mole at m.p.
Boiling point	239.68°K (239.75°)	ΔH (vaporization)	5581 cal/mole at b.p.
Vapor pressure of solid	$\log_{10} p_{cm} = -\frac{1630.70}{T} + 9.00593$		

TABLE 33 (*Cont.*)

Vapor Pressure of Liquid

$$\log_{10} p_{\mathrm{cm}} = -\frac{1612.500}{T} - 0.012311T + 1.2521 \times 10^{-5}T^2 + 10.83997 \quad (T < 240°\mathrm{K})$$

$$\log_{10} p_{\mathrm{mm}} = 12.465400 - \frac{1648.6068}{T} - 0.01638646T + 2.403276 \times 10^{-5}T^2 - 1.168708 \times 10^{-8}T^3 \quad (183.1° < T < 343.1°\mathrm{K})$$

t(°C)	Press. (mm)	t(°C)	Press. (mm)
−80	37.6	0	3221.0
−60	164.2	20	6428.5
−40	538.3	25	7520.5
−20	1426.8	30	8749.0

Triple point pressure... . 4.558 cm

Critical pressure......... .. 112.3 atm Critical temperature.... ..... 406 0°K

Molal Heat Capacity

T(°K)	C_p (cal/deg)	T(°K)	C_p (cal/deg)
90	5 612	190(s)	11.71
120	7.497	200(l)	17.58
150	9.272	220	17.90
170	10 42	240	18.12

Entropy, $S^{\circ}_{298.1}$:

Experimental	45.94 cal/deg/mole
Spectroscopic......	46 03 " " "

Density of Liquid

t(°C)	Density (g/ml)	t(°C)	Density (g/ml)
−70	0.7253	−10	0.6520
−50	.7020	0	.6386
−30	.6777	20	.6103

Viscosity and Dielectric Constant of Liquid

t(°C)	Viscosity, Poise	Dielectric Constant
−60 ± 10		26.7
5	0.001618	18.94
15	.001457	17.82
25	.001350	16.26

Aqueous ammonia solutions

Ammonia is very soluble in water, about 700 volumes of gas per volume of water at 20° being required to give an NH_3 pressure of 1 atm. The densities and partial pressures of some ammonia solutions are given in Table 34 [densities, *International Critical Tables*, Vol. III, p. 59; vapor pressures, Sherwood, *Ind. Eng. Chem.*, **17**, 746 (1925), Scheffer and de Wijs, *Rec. trav. chim.*, **44**, 654 (1925)].

TABLE 34
THE DENSITIES AND PARTIAL AMMONIA PRESSURES OF AMMONIA SOLUTIONS

At 20°C

Weight Per Cent NH_3	Normality (moles NH_3/l soln.)	Density (g/ml)	NH_3 Pressure (mm Hg)
1	0.584	0.9939	—
2	1.162	.9895	12.5
4	2.304	.9811	26.1
8	4.534	.9651	60
12	6.694	.9501	100
16	8.796	.9362	156
20	10.84	.9229	227
24	12.82	.9101	322
28	14.76	.8980	447

At 25°C

Normality	NH_3 Press. (mm)	Normality	NH_3 Press. (mm)
0.0618	0.79	1.005	13.46
.1883	2.41	1.242	16.94
.339	4.41	1.618	22.38
.601	7.96		

The phase diagram of the system NH_3 and H_2O is shown in Fig. 21 [Postma, *Rec. trav. chim.*, **39**, 515 (1920); Elliott, *J. Phys. Chem.*, **28**, 887 (1924)]. The compounds NH_4OH and $(NH_4)_2O$ are seen to exist in the solid form, but they are unstable at room temperature. Water solutions of ammonia contain ammonium hydroxide, a weak base; $NH_4OH = NH_4^+ + OH^-$, $K = 1.65 \times 10^{-5}$ at 25° [Everett and Wynne-Jones, *Proc. Roy. Soc.* (Lond.), **A 169**, 190 (1938)].

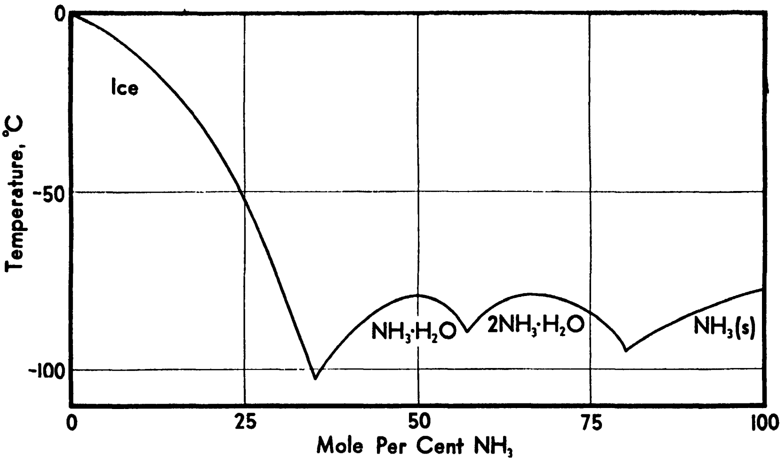


Fig. 21. **The Phase Diagram of the System $H_2O—NH_3$.**

Liquid ammonia solutions

Pure liquid ammonia is of particular chemical interest because of its solvent power for many salts and even some metals. Liquid ammonia solutions have been studied more than those of any other nonaqueous solvent, and important extensions of the concept and theory of solutions have been made. Probably the most unusual and interesting liquid ammonia solutions are those of the metals.

Metal-in-ammonia solutions

It is a remarkable fact that liquid ammonia will dissolve the alkali and alkaline earth metals with the formation of colored solutions. The color of dilute solutions is a lively, beautiful blue. This fact may be easily demonstrated by dissolving a milligram of sodium in 10 ml of liquid ammonia at the temperature of solid CO_2 (dry ice); the metal dissolves quite readily. If the concentration of metal in the solution is high, the liquid has a metallic, copper-like appearance and reflects light at perpendicular incidence much more than do ordinary liquids or nonmetallic solutions.

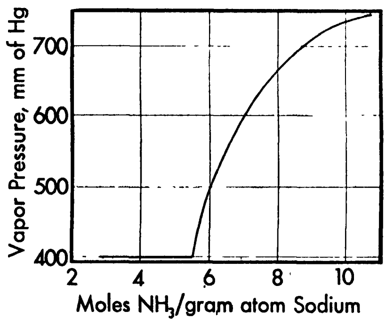


Fig. 22. The Vapor Pressure of Ammonia above Solutions of Sodium in Liquid Ammonia at −33.8° C. [Kraus, Carney, and Johnson, *J. Am. Chem. Soc.*, **49**, 2206 (1927).]

Repeated experiments have shown that, if the ammonia is evaporated from a freshly prepared alkali metal solution, the residue consists of the original metal; that is, there is no chemical change which is not readily reversible. The nonexistence of compounds is also indicated by the vapor pressure curve of sodium in ammonia shown in Fig. 22. If, however, the solution is allowed to stand for some time, the blue color fades and the solution becomes colorless. On evaporating this solution, a white solid residue of an amide, for example $NaNH_2$, remains; it may also be shown that the decrease in the intensity of the blue color is accompanied by the evolution of hydrogen,

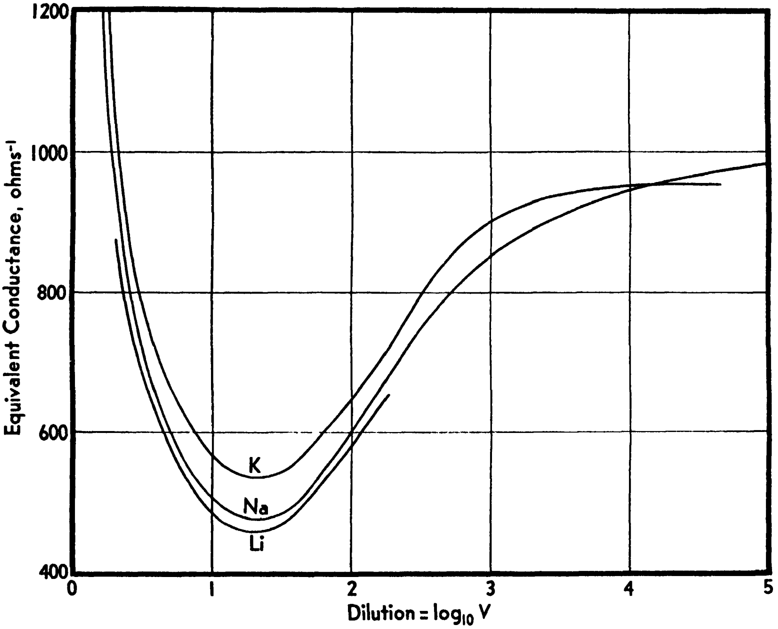


Fig. 23. The Equivalent Conductance of Solutions of Potassium, Sodium, and Lithium in Liquid Ammonia at −33.5° C. V = liters of pure ammonia of density 0.674 in which one gram atom of the metal is dissolved.

$$M + NH_3 = MNH_2 + \tfrac{1}{2}H_2$$

The rate of decomposition is increased markedly by substances such as platinum black, Fe_2O_3, NaOH, or $NaNH_2$, which act as catalysts, but may be greatly decreased by careful preparation of the solutions. If pure materials are used with rigorous exclusion of moisture, sodium solutions may be prepared which are stable for a week or two. Potassium solutions are less stable but will not show appreciable signs of decomposition for about eight hours. It is evident that the solutions are sufficiently stable to allow quantitative physical and chemical experiments to be performed.

All of the alkali metals give blue dilute solutions. A quantitative investigation of the absorption spectra of these solutions has shown that the spectra are identical at the same concentrations [Gibson and Argo, *J. Am. Chem. Soc.*, **40,** 1327 (1918)], and this indicates that the blue color is due to the same substance or ion in all cases. The solutions are good conductors of electricity at all concentrations; the equivalent conductances, Λ, of solutions of sodium, potassium, and lithium as measured by C. Kraus are shown in Figs. 23 and 24 [Kraus, *J. Am. Chem. Soc.*, **43,** 749 (1921)].

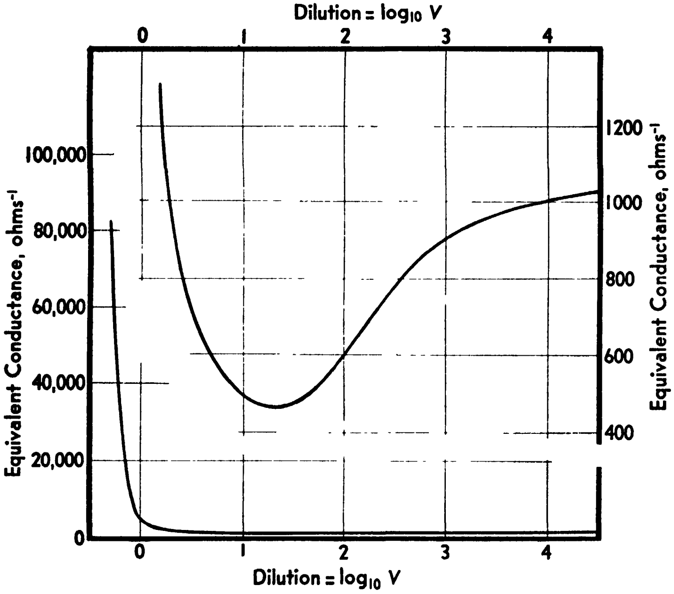


Fig. 24. The Equivalent Conductance of Sodium in Liquid Ammonia at −33.5° C. V = liters of pure liquid ammonia of density 0.674 in which one gram atom of sodium is dissolved.

From both the data and the curves, three characteristics of these solutions are immediately evident: (1) at all concentrations the equivalent conductance is greater than that found for any known salt in solution in any known solvent; (2) the conductance for concentrated solutions is extremely high and of the same order of magnitude as that found for metals (the specific conductance of mercury is 1.036×10^4 reciprocal ohms; that of a saturated solution of sodium in liquid ammonia, 0.5047×10^4); and (3) the conductance goes through a minimum and then increases with dilution to a limiting value. The behavior of the conductance at the higher dilutions is much the same as that found for ordinary salts in water or liquid ammonia. These results, especially the magnitude of the conductance, indicate strongly that the conducting ion or ions are not of the same kind as those responsible for the conductance of ordinary salt solutions in liquid ammonia or other solvents.

In further studies on the mechanism of the conductance, Kraus determined the electromotive force of concentration cells of the type

$$\text{Pt, Na}[C_1\text{, in NH}_3\text{ (l)}]\text{; Na}[C_2\text{, in NH}_3\text{ (l)}]\text{, Pt}$$

and since the observed E.M.F. is dependent not only on the concentrations C_1 and C_2 but also on the transference numbers involved, he was able to show that the negative carrier carried from 7 to 280 times the current carried by the positive ion [*J. Am. Chem. Soc.*, **30,** 1197 (1908); **36,** 864 (1914)]. On the basis of these experiments, Kraus assumed the following equilibria:

$$\text{Na (in liq. NH}_3) = \text{Na}^+ + \text{E}^-$$
$$\text{E}^- + \text{nNH}_3 = (\text{NH}_3)_n\cdot\text{E}^-$$

From the electromotive force measurements, he calculated that at $C_1 = 1.014$ n and $C_2 = 0.6266$ n only about two-thirds of the negative ions were associated with ammonia molecules. He also made vapor pressure measurements on the sodium-in-ammonia solutions to determine, using Raoult's law, whether the effective concentration of the solute was greater than, equal to, or less than the formal concentration. For solutions about 0.2 n, the apparent molecular weight of sodium in solution turned out to be about 23, which is equal to the atomic weight; but at 0.1519 n, the apparent molecular weight was found to be 21.58. Although the applicability of Raoult's law is somewhat doubtful for these solutions, the value indicated some 12% dissociation.

All these facts could be correlated, qualitatively, at least, by the assumption that sodium atoms, sodium ions, free electrons, and solvated electrons were present in equilibrium in the solution. The high conductance in concentrated solutions would be explained by the free electrons, the subsequent decrease to a minimum by the increasing solvation of the electrons. The final rise in very dilute solution, in which solvation of the electrons would be virtually complete, would be due to the increasing dissociation of the sodium atoms present. This theory explains many facts well; but in spite of its qualitative success, further investigations, both theoretical and experimental, have shown that it cannot be correct in some major respects.

The first disagreement came from a theoretical study by L. Farkas [*Z. phys. Chem.*, **A 161,** 355 (1932)] of the electrical conductance of sodium in liquid ammonia. Farkas proceeded on the assumption that the electrons are *restrictedly* free at all concentrations. At low concentrations the conductance is expressed by the formula of Kohlransch for completely ionized strong electrolytes, $\Lambda_c = \Lambda_0 - a\sqrt{C}$. In the more concentrated solutions, where the conductance increases with such extraordinary rapidity, Farkas regarded the conductance as involving "non-mechanical" transfer or jump of electrons from one metal atom to the next. In the theory, the electrons on the metal atoms are required to penetrate a potential barrier, Fig. 25, in passing from one atom to the next, and the probability that this will occur may be calculated from the quantum theory. An important assumption in the theory is that the sodium atoms form an ordered structure in the solution. Since an electric field is present between the electrodes, the probability that the electrons will go through the barrier in the direction of the anode is greater than for the opposite direction. A net flow or passage of electrons through the solution results. Farkas derived the following expression for the conductance of the metal in ammonia solutions:

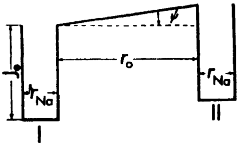


Fig. 25. An Assumed Potential Energy Curve for the Electrons in Concentrated Sodium-in-ammonia Solutions.

$$x = \frac{3 \times 10^{11}}{J_0^{1/2}} 10^{-(4\ 2 \times 10^{8} J_0^{1/2})/C^{1/3}}$$

where $1000x/C = \Lambda$ is the equivalent conductance, C is the concentration in moles per liter of solution, and J_0 is an ionization potential (see Fig. 25) which is evaluated from one experimental value of x. The theory is in moderately good agreement with experiment for solutions containing from one to five moles of sodium per liter of solution.

The most conclusive evidence for rejecting equilibria (such as $\text{Na} = \text{Na}^+ + \text{E}^-$) requiring an appreciable concentration of un-ionized sodium ions or solvated electrons in solution comes from magnetic-susceptibility measurements. If the electrons are not free but are bound to sodium atoms or to ammonia molecules, the solutions would be paramagnetic and the volume susceptibility would depend on the temperature and concentration, in accordance with Curie's law

$$\kappa = \frac{N\mu_0^2 J(J + 1)g^2}{V3kT}$$

when N/V is the number of metal atoms or ammonia ions NH_3^- per unit volume of solution, μ_0 is one Bohr magneton, k is Boltzmann's constant, J is the resultant spin-orbital momentum quantum number of the electron, and g is the Landé factor,

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}.$$

At a concentration approximately that at which a minimum in conductance is observed ($\approx 0.2n$), the contribution of neutral atoms would be at a maximum, according to the Kraus theory. Actually, it is observed that in this region the susceptibility is very low and in fact is negative (corresponding to diamagnetism) at lower temperatures. The temperature coefficient of the susceptibility is very small. From the low value at medium concentrations, the susceptibility per mole of sodium rises until in highly dilute solution it is equivalent to a magnetic moment of one Bohr magneton per sodium atom [Freed and Thode, *Nature*, **134,** 774 (1934); Huster, *Ann. Physik,* **33,** 475 (1938)].

This observed behavior is qualitatively what would be expected if all the electrons were free or under the influence of a periodic (in space, not time) potential field of the sodium atoms. At high concentrations they would then constitute a degenerate Fermi gas with a susceptibility practically independent of temperature, but at lower concentrations the degeneracy would be lifted, with a corresponding rise in the susceptibility. The theory of an electron gas has been developed by Pauli [*Z. Phys.*, **41,** 81 (1927)] and by Bloch [*Z. Phys.*, **53,** 216 (1929)], who derived the following formulas for the volume susceptibility, κ:[1]

Free electrons:

At low temp.[2] .... $\kappa = \mu_0^2\{12(\pi/3)^{2/3}(N/V)^{1/3}m/h^2 - (64\pi^4/9)Vm^3k^2T^2/Nh^6\}$

---

[1] The Pauli-Bloch formula is derived as follows: The Fermi-Dirac distribution law is

$$n_i = \frac{1}{e^{\beta + \frac{\epsilon_i}{NkT}} + 1}$$

with $\epsilon_i = \epsilon_t + \epsilon_m$, where ϵ_t is the translational and ϵ_m the magnetic energy of an electron in a magnetic field, H. In terms of the quantum numbers n_1, n_2, n_3, m_j, j, l, s, and the weight factor

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$

we have

$$\epsilon_t = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right),$$

$abc = V$, the volume; $\epsilon_m = -m_j g \mu_0 H$. The magnetic moment, M, of the system of electrons will be

$$MH = -\sum_{m=-j}^{+j} n_m\epsilon_m = -\frac{4\pi mV}{h^3}\sqrt{2m}\,(kT)^{3/2}\sum_{m=-j}^{+j}\epsilon_m\int_r^{\infty}\frac{x^{1/2}dx}{e^{\beta+x+\epsilon_m/kT}+1}$$

With $j = s = \frac{1}{2}$, $l = 0$, $g = 2$. $\kappa = I/H = M/HV$, we get, after an approximate evaluation of the integrals, the Pauli-Bloch relations. m = mass of the electron.

[2] The second term on the right containing T^2 is usually very small. For an electron gas $\kappa = 2.20 \times 10^{-14}(N/V)^{1/3} - 1.03 \times 10^7(V/N)T^2$; and, since $N/V = 2.6 \times 10^{22}$ for metallic sodium, $\kappa = 6.6 \times 10^{-7} - 3.9 \times 10^{-16}T^2$. That is, κ is prac-

At high temp.......... $\kappa = N\mu_0^2/VkT$

Electrons in a periodic field:

At low temp..... .. $\kappa = K_2\mu_0^2N/V\beta$ $K_2 \cong 1$;
β = exchange energy of electron going from one potential hole to a neighboring one.

At high temp.......... $\kappa = N\mu_0^2/VkT$

The equations may be otherwise stated in the following manner: At low temperatures and high concentrations, all of the lowest states in which the electrons can exist are filled, and in these states the electrons are paired. Only the relatively small number in the higher states are unpaired and able to contribute to the magnetic susceptibility, that is, able to orient themselves in a magnetic field. At high temperatures or low concentrations, respectively, more electrons can be in the higher states, or there are not enough electrons altogether to fill all available states. The concentration of electrons (one electron per atom is regarded as free) in metallic sodium is about 42 moles per liter, while concentrations of sodium in liquid ammonia as low as 0.0022 moles per liter can be studied as to their magnetic properties, a decrease of 20,000 fold. The theory does not give quantitative agreement with the observed susceptibility even in the case of the alkali metals, but it does explain the essential features of the phenomena, namely, that the paramagnetism is small and nearly independent of the temperature. Observed and calculated values are shown in the following table [Klemn and Hauschulz, *Z. Electrochem.*, **45**, 346 (1939)]. The value for a concentrated solution of sodium in liquid ammonia is given also [Huster, *Ann. Physik.*, **33**, 477 (1938)]; the agreement between experiment and theory is as satisfactory as for the pure metals.

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tically independent of temperature. For most metals and solutions of metals in liquid ammonia, $N/V = 10^{22}$ to 10^{16}; only in the latter case does the second term become important.

The κ is the volume susceptibility; χ_m, the molal susceptibility, is the molar volume times κ. Substituting in the low-temperature expression for κ and omitting the small second term, we get

$$\chi_m = 1.86 \times 10^{-6} V^{2/3}$$

where V is the volume available to one mole of electrons. This is the paramagnetic susceptibility. Lande [*Z. Physik*, **64**, 629 (1930)] has shown that free electrons should exhibit a diamagnetism equal to one-third the paramagnetism. The resultant molal susceptibility is then

$$\chi_m = 1.25 \times 10^{-6} V^{2/3}$$

This is the formula used to calculate the χ_m (calc.) in Table 35.

TABLE 35

THE MOLAL SUSCEPTIBILITIES OF THE ALKALI METALS

Metal	χ_m (obs.) $\times 10^6$	Diamagnetic Correction for Cation	Electron Gas	
			χ_m (obs.) $\times 10^6$	χ_m (calc.) $\times 10^6$*
Li....	5	−1.2	6.2	7
Na..........	15	−6	21	10
K..........	21	−15	36	16
Rb........	19.5	−22	41.5	19
Cs...........	30	−35	65	22
Na in liq. NH_3 (sat. soln.).			80	43

* Allowing for the Lande diamagnetism; see footnote on p. 142.

Careful measurements on solutions of sodium in ammonia have been made by Huster [*Ann. Physik*, **33**, 477 (1938)] and on potassium in ammonia by Simon Freed and Nathan Sugarman [Sugarman, Ph. D. Thesis, University of Chicago, 1941]. The essential results of the two investigations were the same; the more accurate work of Freed and Sugerman is shown in Fig. 26 and Table 36. Potassium solutions have an advantage over sodium solutions in that the susceptibility is greater at a given concentration:

TABLE 36

THE MOLAL SUSCEPTIBILITY OF POTASSIUM IN LIQUID AMMONIA

At −33°C		At −53°C	
NORMALITY	$\chi_m \times 10^6$	NORMALITY	$\chi_m \times 10^6$
0.00341	1268	0.00354	809
.00384	1180	.00422	790
00406	1240	.00501	834
.00481	1180	.00844	488
.00812	974	.0331	232
.00960	853		
.03180	402		

At 0.02 n	At 0.01 n
$\chi_{Na} = 400 \times 10^{-6}$	$\chi_{Na} = 650 \times 10^{-6}$
$\chi_K = 550 \times 10^{-6}$	$\chi_K = 825 \times 10^{-6}$

In Fig. 26 is shown also the susceptibility of an ideal electron gas; the values were calculated by Freed and Sugarman using the results of a numerical integration of the Fermi integral [Mott, *Proc. Camb. Phil. Soc.*,

32, 108 (1936)]. The Lande diamagnetism [Lande, *Z. Physik*, **64,** 629 (1930)] was omitted. It is seen that the two curves do not agree either quantitatively or qualitatively; the temperature coefficient predicted by the electron gas theory even has the wrong sign According to the Lande theory, the maximum molal susceptibility for free electrons would correspond to a magnetic moment of only two-thirds of a Bohr magneton per electron, owing to induced diamagnetism cancelling one-third of the normal paramagnetism. It is especially important that experimental points were obtained above the two-thirds value.

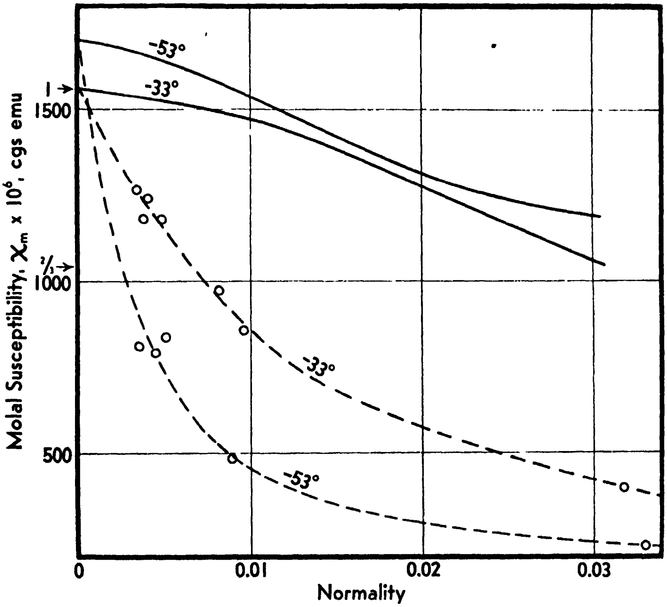


Fig. 26. The Molal Susceptibility of Potassium in Liquid Ammonia. Circles are experimental points; the solid curves give the calculated values for a free electron gas obeying the Fermi-Dirac statistics. The arrow marked *1* represents the limiting paramagnetic susceptibility ($N^2\mu_0^2/RT$) of a mole of free electrons, and the arrow marked ⅔ represents the limiting values ($\frac{2}{3}N^2\mu_0^2/RT$) for the electrons after the Landau diamagnetism is subtracted; T = 240° K.

Similar results were obtained on solutions of sodium. Huster explained his data by assuming the existence of Na_2 molecules in the solution. A similar explanation may be used for potassium; the greater accuracy of the results allows equilibrium constants to be calculated for the reaction $K_2 = 2K^+ + 2E^-$. Constants calculated by using either the Fermi-Dirac statistics or the classical statistics for the electrons are found to be equally satisfactory [Sugarman, personal communication]. It seems, therefore, that the early hopes of obtaining experimental evidence about an electron gas from metals-in-ammonia solutions are not to be fulfilled.

Further evidence as to the condition of the electrons in ammonia solution comes from photoelectric measurements on sodium-in-ammonia solutions [Häsing, *Ann. Physik,* **37,** 509 (1940)]. It is found that the spectral distribution of the quantum yield for concentrated solutions is similar to that for the solid alkali metals. The curve for the blue dilute solutions, however, is different, and large quantum yields are evidence for a volume effect. These facts indicate a different energy distribution for the electrons in the dilute solutions and support the theory that the majority of the electrons, at least, are bound to some center, such as an ammonia molecule. The optical evidence is thus consistently against free electrons, as neither quantum mechanics nor classical optical theory can explain the observed absorption of light on the basis of free electrons.

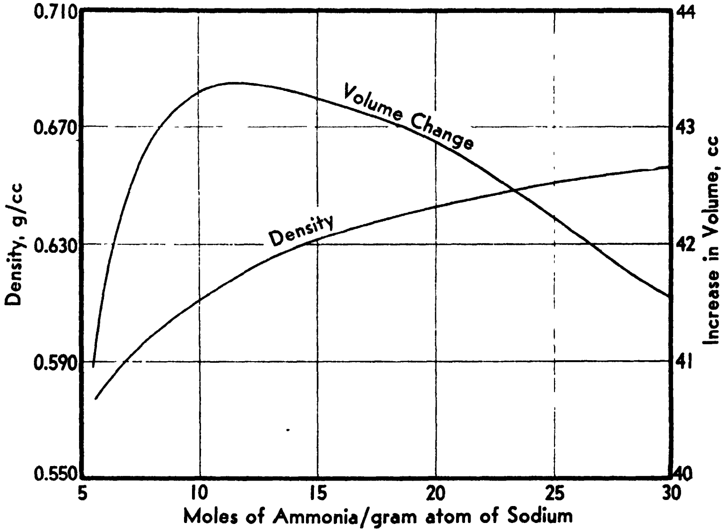


Fig. 27. The Density and Volume Change for Solutions of Sodium in Liquid Ammonia at −33.8° C. The increase in volume is the increase above the sum of the two components.

Although no completely satisfactory theory can yet be given, the situation may be summarized as follows: All evidence shows that the concentrated metal-in-ammonia solutions behave essentially as a metal. In the dilute solutions it is probable from magnetic evidence that an equilibrium, $M_2 = 2M^+ + 2E^-$, exists. The optical evidence indicates that the electrons are solvated, although it is difficult to explain the high conductivities with this assumption. Cell measurements show that the mobility of the negative particle is very much greater than that of the positive particle. The explanation of the exact state of the electrons in the metal-in-ammonia solutions still remains an unsolved problem.

The metal-in-ammonia solutions show rather abnormal behavior with respect to other than electrical properties. For example, the volume of the solutions is greater than the sum of the volumes of the sodium and ammonia composing them; this behavior is shown in Fig. 27 [Kraus, Carney, and Johnson, *J. Am. Chem. Soc.*, **49**, 2206 (1927)]. Ordinarily the volumes of the constituent substances are greater than the volume of the solution. It is to be noted also that the volume change goes through a maximum.

The solubilities of the alkali metals in liquid ammonia do not change rapidly with the temperature, thus indicating that the heat of solution to form saturated solutions is not very great. This behavior has been regarded by some as evidence for the assumption that the solutions are colloidal in nature. Attempts have also been made to explain the absorption spectrum on that assumption [Kruger, *Ann. Physik*, **33**, 265 (1938)], but the evidence for a colloidal solution does not appear to deserve serious consideration [Freed and Thode, *J. Chem. Phys.*, **7**, 85 (1939)]. The solubility data are presented in Table 37.

TABLE 37

SOLUBILITIES OF THE ALKALI METALS IN LIQUID AMMONIA

(The solubilities are in moles NH_3/mole alkali metal.)

Lithium[a]

t(°C)	Solubility	Vapor press. (mm)
0	3.60	34.0
−33.2	3.75	3.4
−63.5	3.81	1.1

Sodium[b]		**Potassium**[c]	
t(°C)	Solubility	t(°C)	Solubility
0	5.79	0	4.68
−33.8	5.48	−33.5	4.95
−50	5.39	−50	5.05
−70	5.20		
−105	4.98		

[a] Johnson and Piskur, *J. Phys. Chem.*, **37**, 93 (1933).

[b] Ruff and Geisel, *Ber.*, **39**, 831 (1906).

[c] Johnson and Meyer, *J. Am. Chem. Soc.*, **54**, 3621 (1932).

Extensive reviews on the solutions of metals in liquid ammonia have been published by Kraus [*The Properties of Electrically Conducting*

Systems, Chap. XIV, Chemical Catalog Co., New York, 1922], by Johnson and Meyer [*Chem. Rev.*, **8,** 273 (1931)], and by Fernelius and Watt [*Chem. Rev.*, **20,** 195 (1937)].

The alkali metals also dissolve in methyl amine, but to a much smaller extent than in ammonia. In that solvent, the equivalent conductance goes through a minimum just as when the solvent is liquid ammonia; the equivalent conductance is much lower and the positions of the minima are not the same as in the ammonia system, however [Gibson and Phipps, *J. Am. Chem. Soc.*, **48,** 312 (1926)].

It has already been stated that the residue that remains on distillation of the metal-in-ammonia solutions consists of the original metal. The alkaline earth metals show a somewhat different behavior in that the residue may consist of a pure type of coordination compound. Thus calcium, strontium, and barium form the coordination compounds $Ca(NH_3)_6$, $Sr(NH_3)_6$, and $Ba(NH_3)_6$, respectively, at about −33° [Biltz and Huttig, *Z. anorg. Chem.*, **114,** 241 (1920)]. These substances have the properties of metals in appearance and in being good electrical conductors. They are not extremely stable, since at higher temperatures the equilibrium pressure of ammonia is sufficient to permit its complete removal. Lithium is intermediate in properties between the other alkali metals and the alkaline earth metals. It is probable that it forms the compound $Li(NH_3)_4$, although it is very unstable. The density of a saturated lithium-in-ammonia solution at 19° is only 0.477 g/ml, making it the lightest known liquid at room temperature. The solution (or compound, $Li(NH_3)_4$) has a melting point of −181 ± 3°, and the equilibrium pressure of ammonia does not reach one atmosphere until about 70° [Jaffe, *Z. Physik*, **93,** 741 (1935)]. Measurements by Jaffe of the Hall effect proved that the saturated solution corresponded to the solid alkali metal in showing one free electron per lithium atom.

TABLE 38

THE MOLAL SUSCEPTIBILITIES OF CALCIUM AND BARIUM IN LIQUID AMMONIA

Calcium				Barium	
−33°		−53°		−33°	
Normality (g atom Ca/l soln.)	$\chi_m \times 10^6$	Normality (g atom Ca/l soln.)	$\chi_m \times 10^6$	Normality (g atom Ba/l soln.)	$\chi_m \times 10^6$
0.00489	1140	0.00510	978	0.00206	2280
02006	938	0209	271		

Magnetic measurements on solutions of calcium and barium in liquid ammonia reveal a striking difference. The molal susceptibility of barium is that expected on the basis of two electrons per atom, whereas the susceptibility of calcium is much lower and may possibly be explained on the basis of one free electron per atom and an assumed coupling of the Ca^+ ions to give Ca_2^{++}. The measured susceptibilities are shown in Table 38 [Nathan Sugarman, Ph. D. Thesis, University of Chicago, 1941].

It is interesting to note a remark by Gibson and Argo [*J. Am. Chem. Soc.*, **40**, 1327 (1918)] that the spectrum of calcium appears to be different in type from the spectra of the alkali metals. No magnetic measurements have been reported on lithium solutions.

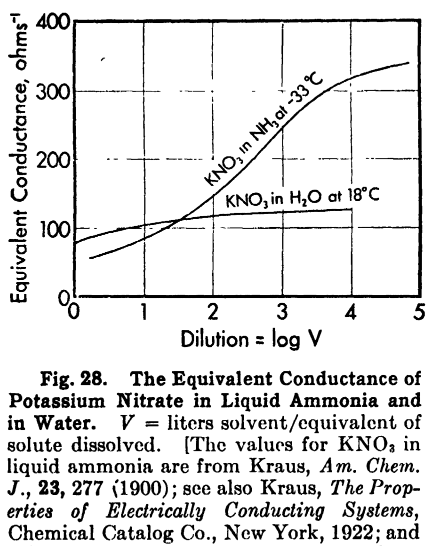


Fig. 28. The Equivalent Conductance of Potassium Nitrate in Liquid Ammonia and in Water. V = liters solvent/equivalent of solute dissolved. [The values for KNO_3 in liquid ammonia are from Kraus, *Am. Chem. J.*, **23**, 277 (1900); see also Kraus, *The Properties of Electrically Conducting Systems*, Chemical Catalog Co., New York, 1922; and Johnson and Fernelius, *J. Chem. Ed.*, **6**, 27 (1929).]

Reactions in liquid ammonia solutions

The general nature of the solutions and reactions in liquid ammonia resembles in many respects that of water. Thus, ordinary salts such as NaCl and KNO_3 will ionize in liquid ammonia solution, yielding the same ions as the corresponding aqueous solutions; the equivalent conductances are quite comparable, as shown in Fig. 28. Metathetic reactions involving insoluble salts are also quite common; thus:

$$Tl^+ + NO_3^- + Na^+ + Cl^- = \underline{TlCl} + Na^+ + NO_3^-$$

That is, when liquid ammonia solutions of $TlNO_3$ and NaCl are mixed, a white precipitate of TlCl is formed. Owing presumably to complex formation, some salts are less soluble in liquid ammonia than in water; $Ca(NH_3)_6Cl_2$, $Na(NH_3)_6Cl_2$, $Zn(NH_3)_6Cl_2$, and $Cd(NH_3)_6Cl_2$, for example, are only slightly soluble in liquid ammonia but dissolve readily in water. On the other hand, silver iodide is very soluble in liquid ammonia but only slightly so in water. Salts of the alkali metals show, as in water, a moderate solubility in liquid ammonia. In order that the solubility relations may be rendered more definite, the following data [Linhard and Stephens, *Z. phys. Chem.*, **A 163**, 185 (1933); Hunt, and

Hunt and Boncyk, *J. Am. Chem. Soc.*, **54,** 3509 (1932), **55,** 3528 (1937)] are presented.

Inasmuch as very little work has been done on solubilities in liquid ammonia, the values in Table 39 must be regarded as provisional for the time being. They do give, doubtless, the order of magnitude, but the absolute values as well as the exact nature of the solid phase need to be confirmed. In the case of the alkali salts, ammonium chloride, and thallous chloride, the solid phases are as given in the table, but definite information is lacking for the remainder of the substances listed.

Table 39

THE SOLUBILITIES OF SALTS IN LIQUID AMMONIA

Solubility in NH_3 at −0.1 ± 0.1° (Moles of salt per 1000 g of NH_3)			Solubility in H_2O at 0° (Moles of salt per 1000 g of H_2O)		
	Na	K		Na	K
Cl	2.20	0.0177	Cl	6.10	3.76
Br	6.21	2.26	Br	7.71	4.49
I	8.80	11.06	I	10.72	7.72
NO_3	15.00	1.04	NO_3	8.62	1.30

Solubility in NH_3 at 25° (In g per 100 g of NH_3)

		NaF	0.35				
NH_4Cl	102.5	NaCl	3.02	KCl	0.04	AgCl	0.83
NH_4Br	237.9	NaBr	137.95	KBr	13.50	AgBr	5.92
NH_4I	368.5	NaI	161.90	KI	182.0	AgI	206.84
NH_4NO_3	390.0	$NaNO_3$	97.6	KNO_3	10.4	$AgNO_3$	86.04
		$NaNH_2$	0.004	KNH_2	3.6		
NH_4ClO_4	137.93						
		NaCNS	205.5				
				KCNO	1.70		
				$KClO_3$	2.52		
				$KBrO_3$	0.002		
				KIO_3	0.000		
		Na_2SO_4	0.00	K_2SO_4	0.00		

Li_2SO_4	0.00	$Ca(NO_3)_2$	80.22	ZnI_2	0.10
$LiNO_3$	243.66	$Ba(NO_3)_2$	97.22	HBO_3	1.92
		$Sr(NO_3)_2$	87.08		

TlCl	0.0260 moles/1000 g NH_3

In aqueous solutions, acids are characterized by the presence of hydrogen ion, H^+, or H_3O^+ (hydronium ion). The corresponding ion in the liquid ammonia system is H^+, or, in much greater concentrations,

NH_4^+. When HCl or NH_4Cl is dissolved in liquid ammonia, it gives in that system an acid. Pure water ionizes into H^+ and OH^-,

$$H_2O = H^+ + OH^-$$

or

$$2H_2O = H_3O^+ + OH^-; \qquad (H^+)(OH^-) = 10^{-14} \text{ at } 25°\text{C}$$

Pure liquid ammonia ionizes as follows [Pleskov and Monoszon, *Acta Physicochim. U.S.S.R.*, **1,** 725 (1935)]:

$$NH_3 = H^+ + NH_2^-$$

or

$$2NH_3 = NH_4^+ + NH_2^-; \qquad (NH_4^+)(NH_2^-) = 1.9 \times 10^{-33} \text{ at } -50°\text{C}$$

The ion analogous to the hydroxyl ion, OH^-, is therefore the amide ion, NH_2^-. Neutralization in the aqueous and liquid ammonia system is represented by the following equations:

$$H^+ + OH^- = H_2O$$
$$NH_4^+ + NH_2^- = 2NH_3$$

and it is an experimental fact that when equivalent amounts of solutions of KNH_2 and NH_4Cl are mixed, the resulting solution contains principally K^+ and Cl^- and only a very small amount of NH_4^+ and NH_2^-. Indeed, the end point of the neutralization can be determined by means of some common indicator such as phenolphthalein. This indicator is colorless in neutral or acid (NH_4^+) solutions and pink in basic (NH_2^-) solutions.

In spite of the fact that the ionization constant of liquid ammonia is very small, some salts will ammonolyze when dissolved in it. Thus, when PbI_2 or $Pb(NO_3)_2$ is dissolved in liquid ammonia, a cloudy solution results which will clear up on the addition of NH_4Cl [see, for example, Franklin, *J. Am. Chem. Soc.*, **27,** 820 (1905); Fernelius and Bowman, *Chem. Rev.*, **26,** 3 (1940)]. A number of elements show amphoteric behavior in liquid ammonia; thus, when a solution of KNH_2 is added to one of AgI or PbI_2, there is first formed a precipitate of $AgNH_2$ or PbNH (both of which are explosive):

$$Ag^+ + NH_2^- = \underline{AgNH_2}$$
$$Pb^{++} + 2NH_2^- = \underline{PbNH} + NH_3$$

Upon the addition of further KNH_2 solution, the precipitate redissolves. The reactions may be written:

$$\underline{AgNH_2} = HAgNH = H^+ + AgNH^-$$
$$\underline{PbNH} = HPbN = H^+ + PbN^-$$

Then,

$$HAgNH + NH_2^- = NH_3 + AgNH^-$$
$$HPbN + NH_2^- = NH_3 + PbN^-$$

That is to say, PbNH and $AgNH_2$ behave both as acids and as bases (imides or amides). This sort of reaction is quite common in the aqueous system, such substances as bivalent lead, aluminum, gallium, zinc, and others being amphoteric; with excess base, they form plumbites, aluminites, and so on. In the aqueous system, compounds of the type $Al(OH)_3$, H_3AlO_2, and Al_2O_3 are possible; in the liquid ammonia system a larger number of analogous compounds exist owing to the circumstance that the ammonia molecule has three replaceable hydrogen atoms, whereas water has only two.

The analogy can be carried still further into the realm of organic chemistry. Thus,

C_2H_5OH	Alcohol
$C_2H_5NH_2$	Amine
$(CH_3)_2O$	Ether
$(CH_3)_2NH$	Dimethyl amine
$(CH_3)_3N$	Trimethyl amine

In fact, it is possible to obtain the organic amines by the simple process of heating together in the presence of a catalyst an alcohol and ammonia.

A number of organic and inorganic compounds of a more complicated nature may be regarded as having analogues in the water and aqueous system. Thus HN_3 is regarded as the ammonia-system analogue of the aqueous acid HNO_3; hydrazine, N_2H_4, might be regarded as the analogue of hydrogen peroxide, H_2O_2, and Na_2CN_2 as that of Na_2CO_3. It must not be forgotten, however, that an analogue is only an analogue and that, while helpful as an aid to the memory and for purposes of classification, it proves nothing.

Oxidation-reduction reactions are fairly common in liquid ammonia solutions. As might be supposed, the metal-in-ammonia solutions are excellent reducing agents [Fernelius and Watt, *Chem. Rev.*, **20,** 195 (1937); Kraus, *ibid.*, **26,** 95 (1940)]. In such solutions may be dissolved S, Se, Te, Sn, Pb, and other elements with the formation of a variety of -ide salts. Thus, the reaction

$$4Na\ (in\ NH_3) + Pb = \underline{Na_4Pb}$$

leads to a white precipitate of Na_4Pb. On the addition of further lead, polyplumbides are formed which are soluble and give green-colored solutions:

$$Na_4Pb + 8Pb(s) = Na_4Pb_9$$

It has been shown [see Kraus, *Chem. Rev.*, **8,** 251 (1931)] that on the electrolysis of a solution of Na_4Pb_9 between lead electrodes, $2\frac{1}{4}$ atoms of lead are dissolved at the cathode and the same number precipitated on the anode for each equivalent of electricity passed through the solution. This compound undergoes a remarkable reaction when a solution of it in liquid ammonia is mixed with one of lead nitrate in the same solvent; metallic lead precipitates, leaving sodium nitrate in the solution.

Sulfur, selenium, tellurium, and tin are reduced to simple -ide and poly -ide salts by metal-in-ammonia solutions. In general the normal salt, for example, Na_2Te or Na_4Sn, is formed at first and is colorless and insoluble. On the addition of further solid oxidizing agent, S, Se, Te, or Sn, the soluble poly -ide salts form, and their solutions show very beautiful colors and color changes as the solids are added. Thus, when solid tellurium is slowly added to sodium-in-ammonia, a white precipitate of Na_2Te forms until all of the sodium has been oxidized; further addition of tellurium results in solutions which are at first green, then yellow-green, yellow, violet-purple, and eventually red when enough has been added to form Na_2Te_4. Tin forms Na_4Sn and, eventually, a bright-red solution of the composition Na_4Sn_8. These experiments are easy to carry out and may be used for lecture demonstrations. It will be recalled that the solution of sulfur in aqueous solutions of sodium sulfide gives the same general type of compound as those just mentioned. It must also be pointed out that the intermetallic -ide compounds may be obtained by melting metallic sodium and the other metal together. The solution-in-ammonia method is in some respects easier and more instructive.

A convenient method for the preparation of some oxides of the alkali metals is the reaction of the metal-in-ammonia with oxygen. Rapid oxidation at $-50°$ of sodium gives Na_2O_2; that of potassium gives quantitative yields of K_2O_2 or KO_2, depending upon how long the reaction is allowed to proceed [Kraus and Whyte, *J. Am. Chem. Soc.*, **48,** 1781 (1926); Kraus and Parmenter, *ibid.*, **56,** 2384 (1934)]. At higher temperatures, the oxides react with ammonia to give the hydroxide, amide, and nitrite. The carbonyls of the alkali and alkaline earth metals, for example, NaCO and $Ca(CO)_2$, are prepared by passing CO through the metal-in-ammonia solution at $-50°$ [Joannis, *Ann. chim. phys.*, [8] **7,** 107 (1906); Pearson, *Nature*, **131,** 166 (1933)]. These carbonyls are white powders which give violent reactions with air and water and decompose explosively on heating:

$$4LiCO = Li_2CO_3 + Li_2O + 3C$$

With carbon dioxide, sodium-in-ammonia at $-50°$ forms H_2NCO_2Na and hydrogen [Rengade, *Compt. rend.*, **138,** 629 (1904)]. Nitrosyl compounds NaNO and $Ba(NO)_2$ are formed by the reaction of the metal and NO [Mentrel, *Compt. rend.*, **135,** 740 (1902); Zintl and Harder, *Ber.*, **66,** 760 (1933)]. The sodium compound is distinct from the hyponitrite, $Na_2N_2O_2$.

Liquid ammonia is not a good solvent for oxidation reactions, as the common oxidizing agents are much less powerful in it than in aqueous solutions. The halogen elements are unstable in ammonia. Nitric and sulfuric acids form ammonium salts which have little or no oxidizing power. Alkali metal permanganates and chromates are soluble and act as rather weak oxidizing agents. An example of an oxidation-reduction reaction is

$$3KNH_2 + 3KNO_3 = 3KOH + N_2 + NH_3 + 3KNO_2$$

This reaction proceeds at a measurable rate at room temperature if a catalyst such as ferric or cobaltic oxide is present [Bergstrom, *J. Am. Chem. Soc.*, **62**, 2381 (1940)]. The further reaction,

$$KNO_2 + KNH_2 = 2KOH + N_2$$

proceeds at an extremely slow rate. No azide is formed, although KN_3 may be prepared in 75% yields by the reaction

$$KNO_3 + 3KNH_2 = 3KOH + KN_3 + NH_3$$

if the solid salts are heated together in a glass tube at 100–130° [Franklin, *J. Am. Chem. Soc.*, **56**, 568 (1934)].

A number of replacement reactions have been studied by Bergstrom [*J. Am. Chem. Soc.*, **50**, 652 (1928) *et ante*]. Some of the reactions are noteworthy because a more noble metal can sometimes be made of replace sodium, the reason for the reversal being due to the formation to very insoluble salts of the noble metal. For example:

$$\begin{aligned} Mg + 2Na^+ + 2I^- &= \underline{MgI_2} + 2Na \text{ (in } NH_3) \\ Al + 3Na^+ + 3NH_2^- &= \underline{Al(NH_2)_3} + 3Na \text{ (in } NH_3) \\ K \text{ (in } NH_3) + Na^+ + Cl^- &= \underline{KCl} + Na \text{ (in } NH_3) \end{aligned}$$

The electromotive series in liquid ammonia solutions has not received a great deal of attention. A few cells have been measured, but all of them have not been free from boundary or liquid-junction potentials of unknown magnitudes. From the existing measurements, the following few members of the electromotive series have been established [Pleskov and Monoszon, *Acta Physicochim. U.S.S.R.*, **2**, 615 (1935)]. The values are all referred to the normal hydrogen electrode potential in the aqueous system as zero. For purposes of comparison, the corresponding normal electrode potentials in the aqueous system are included in the

TABLE 40
ELECTROMOTIVE SERIES IN LIQUID AMMONIA SOLUTION AND WATER AT 20°

Couple	$E°$ in NH_3 (l)	$E°$ in H_2O
K, K^+	2.73 volts	2.92 volts
Na, Na^+	2.59	2.71
Zn, Zn^{++}	1.27	0.76
Cd, Cd^{++}	0.93	0.40
Pb, Pb^{++}	0.42	0.13
H_2, H^+	0.75	0.00
Cu, Cu^{++}	0.32	−0.35
Hg, Hg^{++}	0.00	−0.79
Ag, Ag^+	−0.08	−0.81

table [Cappe and Watt, *J. Chem. Ed.*, **13,** 231 (1936)]. It is evident from the table that in the ammonia system the alkali metals are not such effective reducing agents as they are in the aqueous system.

Two cells free from liquid junctions have been carefully measured, namely, those for which the cell reactions are [Elliott and Yost, *J. Am. Chem. Soc.*, **56,** 1057 (1934); Garner, Green, and Yost, *ibid.*, **57,** 2055 (1935)]:

$$Zn(s) + 2TlCl(s) + 10NH_3(l) = 2Tl(s) + ZnCl_2{\cdot}10NH_3(s) \qquad (E^\circ = 0.8293 \text{ volts})$$

$$Zn(s) + Cd(NH_3)_6Cl_2(s) = Zn(NH_3)_6Cl_2(s) + Cd(s) \qquad (E^\circ = 0.3605 \text{ volts})$$

Unfortunately the compounds involved in these cells are insoluble in liquid ammonia; hence no notion of the normal potentials can be obtained from these measurements. The cell measurements did prove very useful, however, in evaluating the thermodynamic constants of the solid compounds.

The reduction of organic and organic-like substances can sometimes be carried out very effectively in the metal-in-ammonia solutions. This field of investigation appears to have considerable promise in connection with practical applications. The following reactions are representative [see Fernelius and Watt, *Chem. Rev.*, **20,** 195 (1937); Fernelius and Bowman, *ibid.*, **26,** 13 (1940)]:

$$\begin{aligned} RCl + 2Na \text{ (in } NH_3) &= NaCl + RH + NaNH_2 \\ 2RCl + 2Na \text{ (in } NH_3) &= 2NaCl + RH + RNH_2 \\ GeH_4 + Na \text{ (in } NH_3) &= Na^+ + GeH_3^- + \tfrac{1}{2}H_2 \\ Na^+ + GeH_3^- + C_2H_5Br &= Na^+ + Br^- + C_2H_5GeH_3 \end{aligned}$$

CHAPTER 5

Phosphorus, Phosphorus Oxides, and Phosphorus Sulfides

Phosphorus

Preparation

Phosphorus does not occur in the elementary form in nature, and the reduction of its naturally occurring salts requires both a strong reducing agent and high temperatures. The most important sources of this element are the so-called phosphate rocks; the compounds in these rocks that are of principal importance are normal calcium phosphate, $Ca_3(PO_4)_2$, and mixed phosphates, for example, *apatite*, $CaF_2 \cdot 3Ca_3(PO_4)_2$. The phosphate minerals are divided into two classes according to the ease with which they are decomposed by sulfuric acid, the difficultly decomposable ones being known as "hard phosphates" and the others as "soft phosphates." The *coprolites* and *Charleston phosphates* are "soft" calcium phosphates, whereas *Redonda phosphate* ($AlPO_4$) and *vivianite* ($Fe_3(PO_4)_2 \cdot 8H_2O$) are "hard." It should be remarked that there is a large variety of phosphorus-containing minerals, but calcium phosphate and the apatites are at present by far the most important sources of manufactured phosphorus and phosphoric acid. Calcined bones of animals constituted at one time an important source of phosphorus, since they consist principally of "soft" calcium phosphate, but this source no longer suffices for our demands. Fresh bones contain about 58 per cent of normal calcium phosphate.[1]

Phosphorus is ordinarily recovered from minerals in two different ways. In the first, calcium phosphate is digested with sulfuric acid (specific gravity, 1.5), when the reaction

$$Ca_3(PO_4)_2(s) + 3H_2SO_4 = 3CaSO_4(s) + 2H_3PO_4$$

---

[1] In the order of abundance of the elements in the earth's crust (including the atmosphere), phosphorus stands twelfth and is present there to the extent of 0.142 per cent (O, 49.19; Cl, 0.228; P, 0.142; C, 0.139 per cent). Many living things require phosphorus for their existence, and the cycle of its utilization is as important as that of nitrogen. The steps in the cycle are, briefly, absorption of soluble phosphates by plants, conversion of the phosphorus-containing plant substances by animals, return of the phosphorus compounds to the soil, and finally, when necessary, conversion by decomposition to soluble phosphates.

takes place almost completely because of the fact that phosphoric acid is much weaker than sulfuric acid, and the calcium sulfate formed is insoluble in the resulting mixture. The crude phosphoric acid so formed is filtered and then heated with high-pressure steam in coils, the resulting evaporation leading to an acid of from 1.325 to 1.500 specific gravity. This is further purified and sold as such, or is converted to ammonium phosphate; or it may be strongly heated (1050 to 1170°) in a furnace with charcoal, coke, or sawdust and reduced to elementary phosphorus. The effect of the strong heating is twofold: first, it leads to the conversion of the normal or orthophosphoric acid, H_3PO_4, to metaphosphoric acid, $(HPO_3)_n$; second, it causes the reduction of the $(HPO_3)_n$ to P by carbon to take place. The acid method of phosphorus recovery has now given way to the electrical arc furnace process.

In the electrical process, the ground phosphate mineral, calcium phosphate, or apatite, is mixed with coke, C, and silica, SiO_2, and the mixture is placed directly in a furnace heated by means of an electric arc between carbon electrodes. The primary purpose of the arc is to supply heat to raise the temperature of the mixture. The reduction reaction begins at about 1150° and is complete at 1450°. Two steps are involved in the reduction, namely,

$$Ca_3(PO_4)_2(s) + 3SiO_2(s) = 3CaSiO_3(s) + P_2O_5(g)$$

and

$$P_2O_5(g) + 5C(s) = 5CO(g) + 2P(g)$$

Calcium silicate and silica are removed at the bottom of the furnace as a molten slag.

More recent developments of the high-temperature method involve oil burner heating, omission of the silica, and the oxidation of the phosphorus vapors by air to P_2O_5. The fine particles (smoke) of P_2O_5 are not rapidly absorbed by water, but they may be readily precipitated electrically by the Cottrell process and then converted to phosphoric acid or ammonium phosphate without difficulty [Jacob, *Trans. Am. Electrochem. Soc.*, **48**, 277 (1925)]. The oil-heated furnace operates at 1200–1300°. The omission of the silica obviates slag formation with its attendant heat losses and difficulty of removal. The main reactions are

$$Ca_3(PO_4)_2(s) + 5C(s) = 3CaO(s) + 2P(g) + 5CO(g)$$

and

$$2P(g) + \tfrac{5}{2}O_2(g) = P_2O_5(g)$$

No thorough investigation of the equilibrium states of the first reaction appears to have been made.

When phosphorus is recovered in its elementary form by the above reduction methods, the vapors from the furnace are condensed to the liquid state under water. The subsequent treatments to purify it must also be carried out under water in order to avoid rapid oxidation by the air. Pure phosphorus is obtained by fractional distillation in a vacuum or in an atmosphere of nitrogen, or through fractional crystallization from one of the several solvents in which the element is soluble. The form recovered from the furnace and collected under water is known as white or yellow phosphorus, the two colors referring to the same allotropic modification. It is only this form that is appreciably soluble in carbon bisulfide, benzene, ether, and other organic solvents.

Modifications of solid phosphorus

There are several allotropic modifications of elementary phosphorus of which the following have been studied most extensively.

1. *White or yellow phosphorus.* The α or common form of white phosphorus is obtained by the condensation of phosphorus vapors. It is purchasable as soft, yellowish sticks; but when crystallized from solutions or from its vapors, it forms beautiful, transparent crystals of the cubic family. It melts at 44.1°, boils at 280.5°, and reacts readily and sometimes violently with O_2. It is soluble in carbon bisulfide, ether, benzene, and other organic solvents. The β or low-temperature form results when white phosphorus is cooled to the transition temperature, $-76.9°$. It has much the same general appearance as the α form, but its crystals belong to the hexagonal family.
2. *Red or violet phosphorus.* Red phosphorus results when the molten white modification is heated at from 240 to 250° or is exposed to the action of light or X-rays. It is red in color, it is not oxidized at room temperature by O_2, and it is not appreciably soluble in any known solvent Crystals of P (red) are very small.

   Violet or Hittorf phosphorus is obtained as small, violet, monoclinic crystals when a solution of elementary phosphorus in molten lead is cooled. It is believed that the red and violet modifications differ only in their particle or crystal sizes, the crystals of the violet form being larger than those of the red variety.
3. *Black phosphorus.* Black phosphorus is formed when white phosphorus at 220° is subjected to a pressure of 1200 kg/cm^2. It resembles graphite in appearance, is a conductor of electricity (0.711 ohms/cm cube at 0°, graphite 0.0008 ohms/cm cube, tellurium 0.2 ohms/cm cube), and it is somewhat less reactive toward solvents and oxidizing agents than is red or violet phosphorus.

In the following table are assembled, for comparison, some of the more common physical properties of the five best-understood modifications of solid phosphorus.

In addition to these rather definite allotropic modifications, others have been reported from time to time, but for the most part these have

Table 41
SOLID FORMS OF PHOSPHORUS

Color	Density	M.P. (°C)	B.P. (°C)	Inflammability	Solubility
White α......	1.83	44.1	280.5	Very high	Sol. in organic solvents
White β......	1.88	—	—	—	—
Red..........	2.34	≈ 593	—	High	Insoluble
Violet........	2.34	≈ 620	—	High	Insoluble
Black........	2 699	—	—	Low	Insoluble

not been investigated thoroughly enough to permit very definite statements. For example, a black, noncrystalline variety is formed at high pressures but at lower temperatures than those employed to prepare the crystalline black form (see Fig. 29). The noncrystalline form goes over into the violet modification on long heating at 125° [Jacobs, *J. Chem. Phys.*, **5**, 945 (1937)].

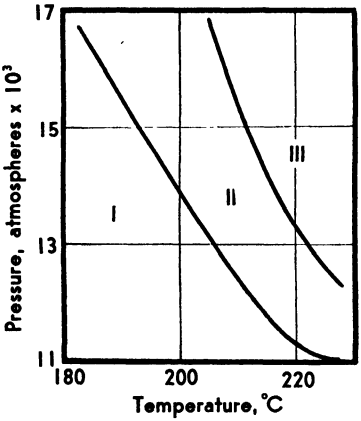


Fig. 29. The Pressure-temperature Diagram for Phosphorus. When white phosphorus is subjected to pressures and temperatures of region I, transition to black noncrystalline phosphorus takes place. Under the conditions of region II or III, the transition is to black crystalline phosphorus; the transition is instantaneous in region III and delayed in region II.

For thermodynamic purposes, white phosphorus is frequently taken as a standard modification, but Latimer [*Oxidation Potentials*] has chosen the red variety for this purpose inasmuch as it is certainly more stable than the white form at room temperature. The black form may be the most stable of all, but this is not absolutely certain. Of interest in this connection is the heat evolved per atomic weight of phosphorus when the various modifications react with bromine in carbon disulfide solution to form solutions of PBr_3. The results shown in the following table were obtained under identical conditions of temperature, amounts, and concentrations [Jacobs, *loc. cit.*]. These results do not prove the black to be more stable than the white or red modifications at room temperature, but they make it appear likely. Entropy measurements would settle this point.

White phosphorus

White phosphorus is characterized by the ease with which it inflames in air or oxygen, by its white or yellowish color and softness, 0.5 (diamond is 10, lead 1.5, silver chloride 1.3, and metallic sodium 0.4), and by its low melting point and the ease with which it supercools. The liquid is clear and colorless if the white phosphorus melted is pure and is protected from excessive light. X-ray diffraction studies show the liquid to contain the element as P_4 molecules; these molecules are tetrahedral with a P-P distance of 2.25 Å [Thomas and Gingrich, *J. Chem. Phys.*, **6**, 659 (1938)].

TABLE 42
HEATS OF REACTION OF SOLID PHOSPHORUS WITH BROMINE IN CS_2 SOLUTION

Modification	Heat of Reaction (cal/at. wt. P)
Black (cryst.)	36,605
Red (commercial)	42,244
Red (from P(w) by heating 6 hrs. at 300° and 6000 atm)	42,507
Black (noncryst.)	44,084
White	(59,500)

The following table contains selected values of the physical properties of solid and liquid white phosphorus [see, for vapor pressures, MacRae and Van Voorhis, *J. Am. Chem. Soc.*, **43**, 547 (1921); Centnerszwer, *Z. phys. Chem.*, **85**, 99 (1913); for energy changes, Bichowsky and Rossini, *Thermochemistry;* Anderson and Yost, *J. Chem. Phys.*, **4**, 529 (1936); for pressure-m.p. and *P*-Trans. data, Tammann, *Wied. Ann.*, **66**, 492 (1898); Bridgman, *J. Am. Chem. Soc.*, **36**, 1344 (1914); for X-ray structures, Hultgren, Gingrich, and Warren, *J. Chem. Phys.*, **3**, 351 (1935); and for heat capacities, Young and Hildebrand, *J. Am. Chem. Soc.*, **64**, 839 (1942)].

TABLE 43
PHYSICAL PROPERTIES OF WHITE PHOSPHORUS
Density

Temperature (°C)	Density (Solid and Liquid)
0	1.83676(s)
20	1.82321(s)
35	1.763(l)
44.4	1.74529(l)
100	1.69490(l)

Surface tension, liquid: 43.09 dynes/cm at 78.3°, 35.56 at 132.1°.
Compressibility of solid at 20° and 100–500 atm: $1/v(\partial v/\partial p)_T = 1.99 \times 10^{-5}\ (\text{kg/cm}^2)^{-1}$.
Index of refraction: 1.8244 for D line at 29.2°.

Table 43 (*Cont.*)

Vapor pressures:

Solid: $\log_{10} p_{mm} = -3297.1/T + 9.6511.$

Liquid: $\log_{10} p_{mm} = -2757.5/T + 7.9515$ for range 50° to 150°.

Solid		Liquid	
Temperature (°C)	Pressure (mm)	Temperature (°C)	Pressure (mm)
20	0.0253	20	0.035
25	.0426	50	.262
44.1	.1810	150	27.2

Melting point, 44.10 ± 0.05°.

Boiling point, 280.5°.

Heat Capacity

$C_{p(\text{solid})} = 21.46 + 0.2872t.$ $0° < t < 44.1°$ cal/deg per mole of P_4.

$C_{p(\text{liquid})} = 24.47 - 0.09521t - 0.00003927t^2.$ $25° < t < 97°$ cal/deg per mole of P_4

$P(s) = P(l),$ $\Delta H_{317.2} = 150.3$ cal/g atom

$4P(s) = P_4(g),$ $\Delta H = 13{,}200$ cal/mole

$\Delta F^{\circ}_{298} = 5700$ cal/mole

Entropy: $S^{\circ}_{298}P(s, w) = 10.1$ cal/deg

Solubility

At room temp., grams in 100 g Solvent (approx.):

Ether	C_2H_5OH	Glycerol	Almond Oil
1.4	.8	.17	1.0

In CS_2, solubity S' in g/100 g solution:

Temperature (°C)	S'
−10	31.40
0	81.27
10	69.80

In C_6H_6, solubility S in g/100 g solvent:

Temperature (°C)	S
0	1.513
20	3.21
30	4.601
40	5.75
81	10.027

Transition Temperatures, α to β Form, as a Function of Pressure

Pressure (kg/cm²)	Temperature (°C)	Δv (cc/g)
1	−76.9	—
6000	−2.4	0.00851
9000	32.7	.000772
12000	64.4	.00694

Tammann found the effect of pressure on the melting point, t_m in °C, of P(α) to be represented by $t_m = 43.93 + 0.0275P - 0.00000050P^2$, when P is expressed in kg/cm². The effect of pressure on the melting point has also been determined by Bridgman [*Phys. Rev.*, **3,** 126 (1914)] with the results shown in the accompanying tabulation.

P (atm)	m.p. (°C)	Δv (cc/kg)
1	44.2	19.3
1000	73.8	17.9
4000	151.3	14.2
6000	196.0	12.0

It has been shown by a number of investigators that, in all the solvents studied, dissolved white phosphorus has the molecular formula P_4; at least, this is true for the not too concentrated solutions. The concentrated solutions in CS_2 may well contain more complicated molecules. White phosphorus also dissolves readily in SO_2(l) and NH_3(l).

Red (violet) and black phosphorus

When molten white phosphorus is heated to 240–250°, it goes over, at a slow or moderate rate, into ordinary solid, red phosphorus; indeed, the methods of manufacture make use of this reaction. Several hours, as high as fifty, are required for complete conversion. A number of substances act as a catalyst for the reaction, of which iodine may be mentioned as an effective one. Thus, with a trace of iodine present, the rate is slow at 100° and almost explosively violent at 200° [Brodie, *J. Chem. Soc.*, **5,** 289 (1853)]. The conversion of the white to the red form is also brought about slowly by light or X-rays. For the preparation of the red form in the pure state, it is necessary to remove the small amounts of white phosphorus that always remain, and this is accomplished by washing or digesting with carbon bisulfide or with lye (NaOH, sp. gr. 1.3). The former reagent acts simply to dissolve the white phosphorus, while the latter reacts with it to form phosphine, hypophosphite, and some hydrogen; the red form is not appreciably affected by either reagent.

Solutions of white phosphorus under the action of heat or light will deposit the red form, and the rate of the reaction depends upon the temperature and other factors. Of interest are the rate measurements made by Schenck with solutions of P(α) in PBr_3 at 184° [*Ber.*, **36,** 979, 4202 (1903); *Z. Electrochem.*, **11,** 117 (1905)]. He found that the rate of the reaction

$$\text{P (in PBr}_3\text{)} = \text{P (red)}$$

is first-order; that is,

$$-\frac{d[\text{P (in PBr}_3\text{)}]}{dt} = k[\text{P (in PBr}_3\text{)}]$$

$$k = 0.0078\ \text{min}^{-1} \text{ at } 184° \text{ and } 0.0048 \text{ at } 172°$$

The mechanism of the reaction may be the following· If it is assumed that the red phosphorus contains more than 4 atoms in the molecule, that is, that it is highly polymerized, then the formation of these higher polymers may require P_2 molecules as an intermediate. Thus the slow first step may be $P_4 = 2P_2$; and this reaction, followed by a series of rapid steps, such as $P_4 + P_2 = P_6$, could lead to the formation of higher polymers. The addition of small amounts of iodine to the solutions catalyzes the reaction.

Violet phosphorus is obtained by heating phosphorus (3 g) with lead (200 g) at 800° in a sealed glass tube for about two days and then allowing the mixture to chill in a freezing mixture. Following this, the glass is removed and the lead is cleaned with hydrofluoric acid. Electrolysis in an acetic acid solution of lead acetate causes the metallic lead to dissolve without affecting the phosphorus, which remains as small violet crystals.

Red and violet phosphorus appear to differ only in crystal size, although the difference does lead to somewhat different physical properties that possibly are to be associated with rate rather than with equilibrium effects; thus, red phosphorus melts at from 592.5° to 610° and the violet form at about 620°. If the violet variety is heated in a closed capillary tube at 620°, it melts to a yellow liquid which begins to deposit red particles at 580° and becomes a solid red mass at 570°. The red modification when melted also yields a yellow liquid which on freezing produces a red solid. The fact that the red and violet forms melt at about the same temperature, and further, the fact that the X-ray pattern for the red, after some heat treatment, is the same as that for the violet form, make it appear probable that the two forms are essentially the same [Hultgren, Gingrich, and Warren, *J. Chem. Phys.*, **3,** 351 (1935)]. X-ray diffraction experiments with red phosphorus show that each atom has three nearest neighbors 2.29 Å away; the next nearest neighbors are 3.48 Å away [Thomas and Gingrich, *J. Chem. Phys.*, **6,** 659 (1938)].

Vapor pressure measurements made on the liquid obtained by melting the white form and on the solid red modification indicate that the pressures may be equal at 589.9°. That is to say, the true melting point of the red variety may be 589.9° instead of 592.5°. Vapor pressure equilibrium is reached only very slowly if at all, however, with the solid red form [see Hittorf, *Phil. Mag.*, **31,** 311 (1865); Stock and Bomolka, *Ber.*, **42,** 4511 (1905)].

t (°C)	P_{atm}
308.5	0.07
346	.13
433.5	1.49
505	8.67
581	36.49
589.5	43 1

The vapor pressures of the solid violet form were determined by Smits and Bokhorst [*Z. phys. Chem.*, **91,** 249 (1916)]. Although equilibrium is very slow of attainment, the results in the accompanying tabulation may have some significance. The vapor pressures of the supercooled and normal liquid from violet phosphorus were determined by the same authors with the results shown in the second tabulation. Inspection of the log P, $1/T$ curves for the solid violet form and the liquid shows their pressures to be equal at about 589.5°, which is regarded as the triple point. This temperature is nearly the same as that found at the intersection of the P (red) − P (liquid) vapor-pressure curves.

The vapor pressures of red phosphorus have also been measured by a dynamic (rate of evaporation) method at low pressures, and very much lower values were obtained [Melville and Gray, *Trans. Faraday Soc.*, **32,** 1026 (1936)]. The difference is believed to be due to the nature of the vapor, which consists at equilibrium of P_4 molecules in the static method, but of P_2 molecules in the dynamic method; that is, it is assumed that P_2 molecules are in rapid reversible equilibrium with the solid, but that the reaction $2P_2(g) = P_4(g)$ is slow and that equilibrium is attained only in the long times involved in the use of the static method.

t (°C)	P_{atm}
504	23.2
545.5	31.9
574	38.8
608	49.0
634	58.6

Critical temp. = 695°
Critical press. = 82.2 atm

The liquid resulting from melting the violet form seems to be the same as that obtained from the white, since the following single equation will reproduce to within ±5% the vapor pressures of both liquids [MacRae and Van Voorhis, *J. Am. Chem. Soc.*, **43,** 547 (1921)] in those parts of the range from 44° to 634°C, in which the liquid exists.

t (°C)	$p \times 10^6$ (mm)
480	5.5
400	6.4
350	3.5
305	1.0

$$\log_{10} p_{mm} = -\frac{2898.1}{T} - 1.2566 \log_{10} T + 11.5694$$

It is not possible to make measurements over the whole range, since the molten white phosphorus goes over into the solid red form at 250°, and the red form does not melt until its temperature is about 600°.

From what has been said above concerning possible failure to establish vapor pressure equilibrium, the reader may gather that estimates of the heats of fusion and vaporization of the violet (red) form are not completely reliable. The values given are, for a temperature of 600°,

$$\begin{array}{lll} \text{P (violet)} = \text{P(l)} & \Delta H = 15{,}600 \text{ cal} \\ \text{4P (violet)} = \text{P}_4\text{(g)} & \Delta H = 25{,}800 \text{ cal} \\ \text{4P(l)} = \text{P}_4\text{(g)} & \Delta H = 10{,}200 \text{ cal} \end{array}$$

The difference in heat contents of the red and yellow forms at room temperature was determined by Giran [*Ann. chim. phys.*, **30,** 203 (1003); see also, Jacobs, *J. Chem. Phys.*, **5,** 945 (1937)], who determined the heat of formation of PBr_3 in carbon disulfide solution using both P(α) and P (red). The result is

$$P(\alpha) = P\ (\text{red}), \qquad \Delta H_{291} = -4{,}200\ \text{cal}$$

A determination of the entropies of the white and red (violet) forms over a range of temperatures would make possible the quantitative evaluation of the relative stabilities of the two modifications and possibly also the transition temperatures.

The compressibility of red phosphorus is $1/v(\partial v/\partial p)_T = 9.2 \times 10^{-6}$ $(\text{kg/cm}^2)^{-1}$ at 20° and 100–500 atm.

Black phosphorus was discovered by Bridgman when he subjected the white form to a pressure of 12,000 kg/cm^2 at 200° [Bridgman, *J. Am. Chem. Soc.*, **36**, 1344 (1914)]. This new form, which resembles graphite in appearance and texture, is a conductor of electricity and is not quite as reactive toward oxidizing agents as the red variety. Unlike red phosphorus, it does not ignite when struck by a hammer. It may be ignited with a match, and it is attacked by cold, concentrated nitric acid. Sulfuric acid does not affect it, and carbon bisulfide does not dissolve it. When heated to about 550°, this black form changes to the red.

The vapor pressures of the crystalline black form are apparently lower than those of the red at some temperatures, according to the measurements of Smits and his coworkers [Smits, Meyer, and Beck, *Proc. Amsterdam Acad.*, **18**, 992 (1915)]:

t (°C)	Black Phosphorus	Red Phosphorus
515	8 5 atm (increasing)	10.5 atm
553	19.3 (increasing)	21.5
567	28.6 (constant)	28 5
578	39.5 (constant)	35.0

But, as these authors remark, in the range where the vapor pressures of P (black) are lower than those of P (red), equilibrium had not yet been attained. Whether or not equilibrium is near, it is impossible to say. The facts indicate but do not prove that the black form is more stable than the red at ordinary temperatures.

The crystal structure of black phosphorus has been shown by Hultgren and his coworkers [*J. Chem. Phys.*, **3**, 351 (1935)] to be one in which the crystal is built up of a succession of indented layers, each phosphorus atom in a layer being equidistant, 2.18 Å, from its three closest neighbors, with an average bond angle of 102°. The nearest approach of atoms in adjacent layers is 3.68 Å. From this fact one can consider each layer to consist of one giant molecule, the adjacent layers being bound together less strongly than neighboring rows of atoms in the same layer. It is noteworthy that the crystal structure of graphite has some features in common with that of P (black), which fact may be correlated with the similarity of texture (flakiness) of the two substances.

The electrical resistivity of black phosphorus is fairly high, 0.711 ohms/cm cube, and decreases with pressure. The temperature coefficient of resistance is also high and negative, namely,

$$\frac{1}{R}\frac{dR}{dT} = -0.0077/\text{deg.}$$

[Bridgman, *Proc. Nat. Acad. Sci.*, **21**, 109 (1935)].

A deep-red form of phosphorus has been mentioned [Birch; see Hultgren *et al.*, *loc. cit.*] as resulting when P(α) is subjected to a pressure of 8000 atm at 300°C. Unlike the black form, it is not flaky.

Phosphorus vapor

All of the early vapor-density measurements on phosphorus were in accord with the assumption of a tetratomic molecule, P_4, and more recent studies confirm this for temperatures somewhat below 800°. At 800° and above, the dissociation of P_4 is appreciable. The vapor densities were thoroughly investigated by Preuner and Brockmöller [*Z. phys. Chem.*, **81**, 129 (1912)] over the temperature range 800–1200°. They made a large number of pressure-temperature measurements on samples of phosphorus enclosed in a quartz bulb equipped with a spiral-quartz-tube manometer, and concluded that the molecules P_4, P_2, and P were present at measurable pressures. Later, Stock, Gibson, and Stamm [*Ber.*, **45**, 3527 (1912)] made a similar study, and their results showed that the partial pressures of monatomic phosphorus were much too small to be observed even at 1200°. Recently Stevenson and Yost [*J. Chem. Phys.*, **9**, 403 (1941)] have evaluated the equilibrium constants for the reaction $P_2(g) = 2P(g)$ from spectroscopic data alone and have shown that the conclusions of Stock, Gibson, and Stamm are correct and that some interfering substances must have been present in the experiments of Preuner and Brockmöller.

The rotation-vibration spectrum of the P_2 molecule is observed in emission when an electrical discharge is passed through the vapor. This spectrum has been carefully analyzed by Herzberg [*Ann. der Physik*, **15**, 677 (1932)] and by Ashley [*Phys. Rev.*, **44**, 919 (1933)]. The vibration levels for the ground electronic state are given in terms of the quantum number v by $\epsilon_{vib.}/hc = 780.76(v + \frac{1}{2}) - 2.98(v + \frac{1}{2})^2$; and the dissociation energy, D_0 (or ΔH_0°), for $P_2(g) = 2P(g)$ has been estimated to be 115,450 cal (5.008 electron volts per mole), with a reported error of $\pm\frac{1}{2}\%$. The phosphorus atoms resulting from the dissociation are in the $4S_{3/2}$ state, which is the lowest electronic energy state. The rotational lines of the molecular spectrum show alternating intensities, the intensity ratio being 3:1, with the odd ($J = 1, 3, 5 \cdots$) levels the more intense. These facts show that the nuclear spin is $\frac{1}{2}$ and, further, that the phosphorus nucleus obeys the Fermi-Dirac distribution law and has therefore an odd number of neutrons and protons. This is in accord with the odd mass number 31 for the single known isotope of phosphorus. The numerical results of Ashley for the rotational constants are:

$$B_v = B_0 - \alpha v = \frac{h}{8\pi^2 cI}$$

$$B_0 = 0.30579 \pm 0.0006 \text{ cm}^{-1}$$

$$\alpha = 0.00165 \pm 0.00003 \text{ cm}^{-1}$$

$$r_0 = 1.88 \text{ Å} \qquad I = 90.47 \times 10^{-40} \text{ g cm}^2$$

where v is the vibrational quantum number.

From the observed energy levels, the partition function may be evaluated. It is defined as

$$Q = \sum_{n=0}^{\infty} \exp\left(-\frac{\epsilon_n}{kT}\right)$$

where ϵ_n is the energy of a single molecule in the nth quantum state; the summation is taken over all accessible quantum states, including translational states. The correlation of thermodynamics and statistical mechanics gives the following formula [see, for example, Tolman, *Statistical Mechanics,* Oxford University Press, 1938].

$$\begin{aligned} \Delta H_0^\circ &= \Delta F^\circ - RT\Delta(\log_e N_0 - \log_e Q) \\ &= -RT \log_e K - RT\Delta(\log_e N_0 - \log_e Q) \end{aligned}$$

(N_0 is Avogadro's number.)

This expression may be used for the direct calculation of equilibrium constants if a spectroscopic value of ΔH_0° is available; or, conversely, ΔH_0° may be calculated from the experimentally measured equilibrium constants. ΔH_0° is independent of T, and its constancy for a series of temperatures is a test of the consistency of the experimental K and Q values; the test is not always sufficiently sensitive, but it is quite useful.

In Table 44 are presented the ΔH_0° values calculated by means of the above equation and the data of Preuner and Brockmöller. It is evident that neither is the ΔH_0° satisfactorily constant nor is it in agreement with the spectroscopically determined value, 115,450 cal/mole. Table 45 contains the values of K_{atm} calculated from spectroscopic data alone; it is believed that these equilibrium constants are much more reliable than those shown in Table 44. It is evident that the dissociation of diatomic phosphorus is extremely slight even at 1200°.

Further evidence for the superiority of Stock, Gibson, and Stamm's equilibrium data appears when the reaction $P_4(g) = 2P_2(g)$ is considered. Electron-diffraction experiments show the P_4 gas molecule to be tetrahedral with the P-P distance equal to 2.21 Å [Maxwell, Hendricks, and Mosley, *J. Chem. Phys.*, **3**, 699 (1935)]. Venkateswaran [*Proc. Ind. Acad. Sci.*, **3**, 260 (1935)] photographed the Raman spectrum of liquid phosphorus and found three lines corresponding to the three allowed fundamentals for a tetratomic, tetrahedral molecule. The frequencies and, in parentheses, their degeneracies are $\omega_{1(2)} = 362\ \text{cm}^{-1}$, $\omega_{2(3)} = 463\ \text{cm}^{-1}$, and $\omega_{3(1)} = 607\ \text{cm}^{-1}$; the frequencies conform approximately to the relation $2\omega_1 = \sqrt{2}\omega_2 = \omega_3$, derived from a simple normal coordinate treatment for a tetrahedral structure. Our information is, then, complete enough to allow the calculation of the partition function. In Table 46 are presented the experimental values of K_{atm} obtained by both Preuner and Brockmöller (PB), and Stock, Gibson, and Stamm (SGS), together with the corresponding ΔH_0° values for the reaction $P_4(g) = 2P_2(g)$. The constancy of the ΔH_0° values obtained using the experimental results of Stock and co-workers is very satisfactory and is to be contrasted with the large and unidirectional variations shown by the ΔH_0° calculated from Preuner and Brockmöller's data. The results of the calculations show quite definitely that the measurements of Stock, Gibson, and Stamm are free from any major errors, and further, that dissociation of diatomic phosphorus is slight even at 1200°.

TABLE 44

ΔH_0° VALUES CALCULATED FROM EQUILIBRIUM AND MOLECULAR DATA

[$P_2(g) = 2P(g)$]

T (°K)	$-\text{Log}_e\ K_{atm}$	$-\Delta H_0^\circ$ (cal)
1073	10.027	49,400
1173	8 061	49,600
1273	6.452	49,900
1373	5.065	50,200
1473	3.859	50,500

TABLE 45

VALUES OF K_{atm} CALCULATED FROM SPECTROSCOPIC DATA

[$P_2(g) = 2P(g)$, $K_{atm} = P_P^2/P_{P_2}$, $\Delta H_0^\circ = 115{,}450$ cal]

T (°K)	$K_{atm} \times 10^{20}$	$-\text{Log}_e\ K_{atm}$
1073	0.74	46.35
1173	91.	41.54
1273	5400.	37.47
1373	17×10^4	33.99
1473	36×10^5	30.96

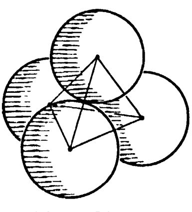


Fig. 30. The Structure of the P_4 and As_4 Molecules. P—P = 2.21Å; As—As = 2.44Å.

From the existing data it was also possible for Stevenson and Yost to calculate a fairly reliable value for the entropy of white phosphorus, P(w). MacRae and Van Voorhis studied the vapor pressures of both white

TABLE 46

THE VALUES OF ΔH_0° FROM MOLECULAR AND EQUILIBRIUM DATA

$[P_4(g) = 2P_2(g),\ K_{atm} = P_{P_2}^2/P_{P_4}]$

T (°K)	K_{atm} (PB)	ΔH_0° (cal)	K_{atm} (SGS)	ΔH_0°
1073	0.00855	48,460	—	—
1173	.0329	49,730	0.00645	53,540
1273	.1053	51,000	.0375	53,590
1373	.2763	52,310	.1671	53,670
1473	.6579	53,440	.6118	53,660

and liquid phosphorus, and their results give

$$4P(w) = P_4(g), \qquad \Delta F_{298}^\circ = 5700 \text{ cal}$$
$$\Delta H_{298}^\circ = 13{,}200 \text{ cal}$$

	S_{298}° (cal/deg)
$P(g)$	38.99
$P_2(g)$	52.15
$P_4(g)$	66.92
$P(w)$	10.1

No correction has been made for gas imperfections. The entropies presented for elementary phosphorus were computed from molecular data and the vapor pressure result. Entropy determinations of the four more common modifications of solid phosphorus, namely, P(w, α), P(w, β), P (red), and P (black), would add considerably to our understanding of this important element.

The oxidation of phosphorus

When white phosphorus at room temperature (16–30°) is exposed to the action of moist air or oxygen at lower-than-atmospheric pressures, a greenish glow is observed. The factors affecting the glow and the reactions taking place with it have been repeatedly investigated; and while a completely satisfactory mechanism for the reaction has not as yet been arrived at, it is significant that the excited molecule PO has been found to be the emitter of at least some of the radiation [Rumpf, *Z. phys. Chem.*, **38B**, 469 (1938)]. If the intensity of the glow is estimated visually as a function of oxygen pressure, then no light is observed with $p_{O_2} = 76$ cm; but on decreasing the pressure of oxygen, the glow will eventually appear at $p_{O_2} \approx 60$ cm, and its intensity will then increase to a maximum with decrease in p_{O_2} and then decrease to zero when $p_{O_2} = 0$. The intensity of the glow is a function of the temperature and the partial pressure of water vapor as well as of oxygen. If an oxygen-water vapor mixture, at less-than-atmospheric pressure, is passed rapidly over white phosphorus at room temperature, the glow no longer comes from the surface of the phosphorus, but appears "downstream" a short distance. It is also known that P_2O_3 glows with O_2—H_2O mixtures. A number of vapors show an inhibiting action on the glow produced, this effect being such that higher temperatures are required to obtain the same glow intensity in their presence than are necessary when such inhibitors are absent. It is also found that when phosphorus and oxygen react in a closed system, the rate of decrease in p_{O_2} with time, dp_{O_2}/dt, is not constant but increases as p_{O_2} decreases.

Experiments have also been made on the ignition temperature of white phosphorus as determined by the pressure of oxygen, water vapor, and unreactive gases. Thus, in air saturated with H_2O at 30.1°, the white phosphorus ignites when its temperature reaches 30°; if the air is saturated with water vapor at 38.1°, then the ignition temperature of the phosphorus is lower, namely, 17°. When water is replaced by organic vapors, the ignition temperature usually increases. Investigations of a more careful nature made on the gas-phase reaction $P_4(g) + O_2$ show that, for a given partial pressure of $P_4(g)$, no ignition results if the oxygen pressure falls below a certain critical value; this critical pressure is a function of the partial pressure of any indifferent gas present, for example, He or Ar.

The facts just cited will serve to give the reader a qualitative notion of the nature of the phenomena observed. A complete mechanism requires a much closer study of the reaction, but it does appear that a chain of intermediate steps is indicated in order to explain the inhibiting action of the oxygen itself as well as that of indifferent gases.

The experimental material may now be examined in somewhat more detail—not with the hope of elucidating completely the mechanism of the oxidation, but rather to exhibit the nature of phenomena themselves; the glow and its effects shall be considered first.

Several investigators have photographed the spectrum of the greenish glow, which, since the intensity is not great, necessitates long exposures up to 95 hours. Ingenious devices for maintaining the glow for long periods have been devised; these depend usually on a means for preventing the temperature of the phosphorus from rising to the ignition point. The spectrum shows a continuum in the visible region (its intensity increasing with the rate of oxidation of the phosphorus) and a series of bands and lines stretching from 3418 Å to 2371 Å. Some fourteen lines or bands were observed by Centnerszwer and Petrikalen [*Z. phys. Chem.*, **80,** 235 (1912); Centnerszwer, *Z. Physik.*, **22,** 119 (1924); see also Hughes, *Proc. Camb. Phil. Soc.*, **15,** 483 (1910); Busse, *Ann. Physik.*, **82,** 873 and **83,** 80 (1927)]; and some of these were shown by Emeleus and Downey [*J. Chem. Soc.*, **125,** 2491 (1924); see also Emeleus and Purcell, *J. Chem. Soc.*, 788 (1927)] to have a resolvable structure. These authors showed that, when the oxidizer is enriched air and the phosphorus is burning, the continuum is most intense and the ultraviolet lines are weaker and stop at 2530 Å. With air at 5 cm pressure, the glow shows a weaker continuum and the lines extend to 2371 Å wave length. When P_2O_3 at 30–40° burns in moist air, the same spectrum is obtained [Emeleus, *J. Chem. Soc.*, **127,** 1362 (1925)]; but this shows only that the emitter is the same in both cases, and not necessarily that the glow owes its origin only to the oxidation of the intermediate P_2O_3. The emitter of some of the band lines has been shown by Rumpf [*Z. phys. Chem.*, **38B,** 469 (1938)] to be phosphorus monoxide, PO, a molecule that does not exist under ordinary conditions, but only in flames or electrical discharges. Phosphorus monoxide is not necessarily the first compound formed in the oxidation of the phosphorus.

Some observers [Downey, *J. Chem. Soc.*, **125,** 347 (1924)] report the formation of ozone during the oxidation of the white phosphorus, and also that the ozone will form in oxygen separated from the glowing phosphorus-oxygen mixture by a fluorite or quartz window. The liberation of iodine from a potassium iodide solution was the test used for showing the presence of ozone. The formation of ozone and the fact that the spectrum of the glow shows ultraviolet radiation up to 2371 Å suggests immediately that shorter wave length radiation capable of being absorbed by O_2 and converting O_2 into O_3 is also emitted. If ozone is formed, it may well play an important role in the reactions that follow the primary light-producing one. It is pertinent to remark that more definite proof for the formation of ozone is desirable; the fact that iodine is liberated from an aqueous solution of potassium iodide by the gas mixture after passing over P(w) provides necessary but not sufficient evidence for the presence of the ozone. The following data (Downey) for the glow intensity and ozone formed as a function of the temperature of the phosphorus and the oxygen pressure give a quantitative picture of the phenomenon. In the experiments, 390 cc. of dry O_2 were passed over the phosphorus for 60 minutes when the phosphorus was kept at 16.6°, and for 30 minutes at 21.8°.

Temp. of Phosphorus	p_{O_2} (mm)	O_3, Relative	Glow Intensity, Relative
16.6°	350	100	100
	290	108	107
	238	120	120
	158	143	142
21.8°	488	734	338
	388	233	123
	290	100	100
	190	113	115

A consideration of the rate of oxidation of white phosphorus by oxygen shows no lack of experimental data, but they have not been obtained under conditions of constant surface and complete mixing. One experiment provides, therefore, a set of measurements which cannot be related quantitatively to the results of another experiment. No measurements appear to have been made in which the gas phase was stirred; hence its composition cannot be regarded as uniform in any of the published results. The following results were obtained by Russell [*J. Chem. Soc.*, **83,** 1263 (1903); see also Kohlschutter and Frumkin, *Ber.*, **47,** 1088 (1914)] in some careful experiments in which the pressure of oxygen above distilled white phosphorus in a closed container was followed with time. He found that very dry and very moist oxygen does not react nearly as rapidly with white phosphorus at room temperatures as does oxygen containing the small amount of water vapor resulting from passing the gas through ordinary concentrated sulfuric acid. Indeed, if p_{H_2O} is around 16–20 mm, its inhibiting effect is very great. This appears to be due to the protecting white layer or crust that forms to a greater or less extent when the moist oxygen first comes in contact with the phosphorus. Reaction does not set in until p_{O_2} = 500 mm,

TABLE 47

THE RATE OF OXIDATION OF WHITE PHOSPHORUS WITH OXYGEN

Temp. = 18.6°

Time (hours)	p_{O_2} (mm)	k_1	k_2	Time (hours)	p_{O_2}[a] (mm)	k_1
0.	669.82	—	—	0	1319.2	—
3.	527.49	346	97.1	1	1273.7	156
4.	468.20	389	106.	2	1231.6	149
5.08	395.12	451	118.	6	1103.0	129
7.	200.42	749	167.	14	874.5	127
7.53	106.87	1058	206.	20	730.0	128
8.08	0.00	1068	335.	22	687.4	129
				25	615.3	132

Temp. = 13.6°, p_{N_2} = 240 mm

Time (min.)	p_{O_2} (mm)	Time (min.)	p_{O_2} (mm)
0	393.42	180	91.93
45	327.14	225	46.93
90	247.54	270	19.38
135	160.05	315	6.30

---

[a] A faint glow, visible only in a dark room, was observed initially; and toward the end of the run, its intensity increased to that ordinarily observed.

while with nearly dry oxygen, reaction takes place at room temperature even with an oxygen pressure of two atmospheres or more. When $p_{H_2O} = 4–5$ mm, the inhibiting action virtually disappears. In considering Table 47 above, it is necessary to understand that rates depend on the surface exposed, and hence will not be the same in two experiments, unless, as is rarely the case, the surfaces are the same. The values of k_1 and k_2 were calculated from the integrated form of the equations $-dp_{O_2}/dt = k_1p_{O_2}$ and $-dp_{O_2}/dt = k_2\sqrt{p_{O_2}}$ for the interval $t = 0$ to $t = t$; to arrive at the constants defined by the differential equations, k_1 and k_2 should be multiplied by 2.3×10^4. The oxygen used was dried by passing through concentrated sulfuric acid or anhydrous calcium chloride. Fig. 31 is a plot of $\Delta p_{O_2}/\Delta t$ against p_{O_2} for the experiment at 18.6°.

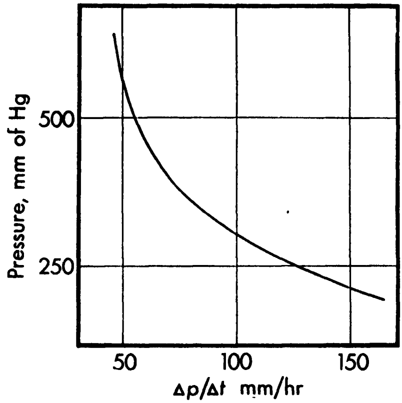


Fig. 31. The Rate of Oxidation of Phosphorus by Pure Oxygen at 18.6° C.

It is at once evident that neither k_1 nor k_2 remains constant in the first, low-pressure experiment; but in the second, high-pressure experiment, k_1 remains quite constant throughout the run. The rate equation should, accordingly, have the form $-dp_{O_2}/dt = k_1p_{O_2}f(1/p_{O_2})$, with $f(0) = 1$ in order that the equation reduce to the proper form for high pressures. When the first-order rate equation is modified to take into account the rate of vaporization of phosphorus, it takes the form $-dp_{O_2}/dt = k_2\sqrt{p_{O_2}}$; but since k_2 is not constant, the assumption of first order or that the oxidation takes place only in the vapor phase must be discarded. It is possible that a chain mechanism would be in better accord with the experimental results.

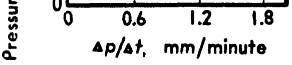


Fig. 32. The Rate of Oxidation of Phosphorus by Oxygen Diluted with Nitrogen at 13.6° C. Initial p_{O_2} = 393.4 mm, p_{N_2} = 240.1 mm.

An examination of the results for the third experiment, in which nitrogen was present, brings out the fact that $-dp_{O_2}/dt$ goes through a maximum at $p_{O_2} = 250$ mm, as shown in Fig. 32. The explanation for this result is believed, by Russell, to depend on diffusion effects. Thus, upon reaction, the concentration of oxygen tends to decrease in the neighborhood of the phosphorus, and this would lead to an increase in $-dp_{O_2}/dt$, if the effect were not offset to some extent by the increase in oxygen concentration resulting from diffusion. Inasmuch as the rate of diffusion decreases with p_{O_2}, we may expect $-dp_{O_2}/dt$ to decrease at low p_{O_2}, since the concentration of O_2 at the phosphorus surface may then become effectively zero. At high and at low partial pressures of oxygen, conditions for a rapid rate are therefore less favorable than at intermediate partial pressures; consequently, there must result a maximum value for $-dp_{O_2}/dt$. It is assumed that no mixing other than by diffusion takes place. Experiments in which O_2—N_2 mixtures were constantly stirred would establish whether or not diffusion is the sole factor in bringing about a maximum in the rate of oxidation.

Experiments on the oxidation of phosphorus vapor are easier to treat theoretically than those involving solid phosphorus, since the number of effective variables is smaller. Investigations by Semenoff [*Z. Physik.*, **46,** 109 (1927)] and by Kowalsky [*Z. phys. Chem.*, **4B,** 288 (1929)] have shown that, for a given pressure of P_4, there is a *critical* pressure of oxygen above which ignition occurs and below which the rate of oxidation becomes quite slow. For the pressures of P_4 obtainable at room temperature, the *critical* pressures of oxygen are less than 1 mm. The *critical* pressure $\overset{*}{p}_{O_2}$ depends upon the pressure of P_4(g) and the diameter, d, of the cylindrical reaction vessel, but is independent of the temperature.

$$p_{O_2}\overset{*}{p}_{O_2}\left\{1 + \frac{p_x}{p_{O_2} + p_x}\right\} d^2 = \text{Constant}$$

where p_x is the pressure of an added indifferent gas such as helium or argon. There is also an upper critical pressure for a given reaction vessel and pressure of P_4(g), that is, a pressure above which no ignition occurs. This upper limit of p_{O_2} is, unlike the lower limit, directly proportional to the pressure of P_4(g). A chain mechanism is suggested by the facts; if the chains are not terminated at the walls of the vessel, they spread until the rapid reaction of ignition results. A large container favors unbroken chains and hence ignition at lower oxygen pressures. The subject has been considered further by Melville and Ludlam [*Proc. Roy. Soc.*, **132A,** 108 (1931); *Trans. Faraday Soc.*, **28,** 814 (1932)], who finds that, for a number of indifferent gases, the critical oxygen and phosphorus pressures, p''_{O_2} and p''_{P_4}, are more accurately related to the critical pressures $\overset{*}{p}_{O_2}$ and $\overset{*}{p}_{P_4}$ when indifferent gases are absent, by the expression

$$\overset{*}{p}_{P_4}\overset{*}{p}_{O_2} = p''_{P_4}p''_{O_2}\left\{1 + \mu\frac{p_x}{p''_{P_4} + p''_{O_2}}\right\}$$

where μ is a constant depending on the indifferent gas ($\mu = 0.13$ for He and 0.84 for CCl_4). In Fig. 33 is shown a graph in which the log p_{P_4} is plotted against the logarithms of the critical oxygen pressures for both the upper and the lower limits. The simple theory of a branching chain reaction [Kassel, *Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co., N. Y., 1932, p. 296] leads to an inequality between the critical pressures of oxygen and phosphorus and the vessel diameter, namely,

$$\frac{k_2}{k_1 d^2}\frac{1}{p_{P_4}} \leqslant p_{O_2} \leqslant \frac{k_1}{k_3}(P_4)$$

where the rate of branching is

$$k_1 N \frac{p_{O_2} p_{P_4}}{p_{O_2} + p_{P_4}}$$

(N is the number of chains in progress) the rate of chain destruction by diffusion to the walls is

$$\left(\frac{k_2 N}{d^2}\right)\frac{1}{p_{O_2} + p_{P_4}}$$

and the rate of loss of chains by collision with oxygen is $k_3 N p_{O_2}$ On the assumption that $p_{O_2} \gg p_{P_4}$, the above inequality follows if the number of chains is to increase indefinitely. These results may well have direct relation to the reaction involving solid phosphorus, but this case appears to be rather more complicated in its details (rate of evaporation of phosphorus, lack of vapor-solid equilibrium, and so forth), and further discussion of it, while of interest, would not be fruitful at this time.

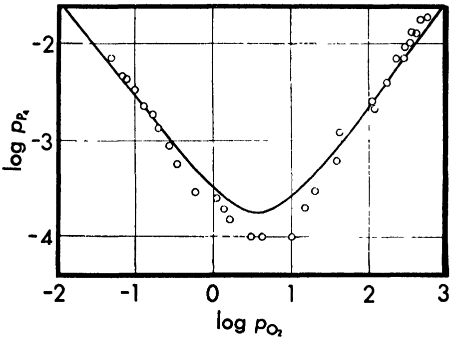


Fig. 33. The Critical Pressures for the Oxidation of Phosphorus Vapor. The curve corresponds to the predictions of the theory; the points are experimental.

There remains the important question as to the oxides formed during the oxidation of white phosphorus. It is known that the slow oxidation at 11° leads to the formation of some PO_2 (that is, P_nO_{2n}), some P_4O_6 (often written P_2O_3), and considerable quantities of P_4O_{10} (often written P_2O_5). Since PO_2 is not volatile and, moreover, does not appear to be oxidized rapidly by O_2, it does not seem to be a likely intermediate in the complete oxidation of P(w) to P_2O_5. Phosphorus trioxide, P_4O_6, is formed in considerable amounts when white phosphorus is burned at 50° in 90 mm of an enriched air (75% O_2, 25% N_2); smaller amounts are formed under other conditions. Since P_4O_6 is volatile, and since it too glows when oxidized to P_4O_{10} with oxygen under proper conditions, it might even be supposed that all of the glow accompanies its oxidation. The fact that the glow with P(w) + O_2 is inhibited somewhat by the presence of P_4O_6 does not add support to the idea. Since excited PO molecules have been found to be responsible for at least some of the radiation observed in the greenish glow, and since this substance doubtless reacts rapidly with oxygen, it may form one of the important intermediates in the oxidation reaction.

The Oxides of Phosphorus

Phosphorus oxides

The well-established oxides of phosphorus are the following:

P_4O_6	Phosphorus trioxide
$P_2O_4(P_nO_{2n})$	Phosphorus tetroxide
P_4O_{10}	Phosphorus pentoxide

There appears to be no reasonable relation between the formulas of the oxides and their names, since the formulas were, at one time, believed to be P_2O_4, P_2O_3, and P_2O_5, respectively. Two other lower oxides, namely, P_4O and P_2O, have been described, but it is not yet certain that they are not simply mixtures of phosphorus and one or more of the known oxides [Chalk and Partington, *J. Chem. Soc.*, 1930 (1927)]. A higher oxide has also been described. It is found that on passing P_4O_{10} vapor mixed with oxygen through an electric discharge, a dark-violet solid is obtained which decomposes above 130°, liberating oxygen. The solid is soluble in water, giving an unstable, strongly oxidizing solution. It is believed to be the anhydride of peroxyphosphoric acid, $H_4P_2O_8$, and is assigned the formula P_2O_6 [Schenck and Platz, *Z. anorg. Chem.*, **233,** 403 (1937)].

Phosphorus trioxide, P_4O_6

This oxide was first studied thoroughly by Thorpe and Tutton [*J. Chem. Soc.*, **57,** 545 (1890); *ibid.*, **59,** 1019 (1891)], who separated appreciable quantities of the substance from the oxidation products of white phosphorus. Their yields were not high, but attempts to increase them have been successfully made by Manley [*J. Chem. Soc.*, **121,** 331 (1922)], and especially by Wolf and Schmager [*Ber.*, **62,** 771 (1929)]. The latter authors investigated carefully the conditions under which maximum yields were obtainable and concluded that best results were obtained when white phosphorus at 46–50° is burned in a 17-mm quartz tube in an enriched air (75% O_2) whose pressure is maintained at 90 mm and whose rate of flow through the tube is 30 l/hour. The yield is about 56 per cent, based on the phosphorus consumed. The raw product always contains some dissolved phosphorus even after repeated distillation, but this is easily removed by illuminating with a mercury arc until all of it is converted into the insoluble red variety. The final purified product forms colorless crystals melting at 23.8° to a clear, colorless liquid which boils without decomposition at 175.4°. Vapor pressures of liquid P_4O_6 have been measured by Doormaal and Scheffer [*Rec. trav. chim.*, **50,** 1100 (1931)], and their interpolated values at even temperatures are shown in the accompanying tabulation.

The dielectric constant of liquid phosphorus trioxide, P_4O_6, is 3.2 at 22°, the surface tension is 36.58 dynes/cm at 34.3°, and the liquid is soluble in organic solvents. In molten naphthalene at about 80°, it has the molecular formula P_4O_6 [see *e.g.*. Schenck, Mihr, and Bathien, *Ber.*, **39,** 1506 (1906)]. In the vapor state the molecules are also P_4O_6; their structure has been investigated by the electron-diffraction method [Hampson and Stosick, *J. Am. Chem. Soc.*, **60,** 1814 (1938)] and is shown in Fig. 34.

t (°C)	p_{mm}	t (°C)	p_{mm}
50	8.1	120	159.8
60	13.6	140	299
70	22.0	160	520
80	34.6	170	668
100	78.3	175	753

$$\log_{10} p_{mm} = -\frac{2860.0}{T} + 11.0516 - 0.00400T$$

$$P_4O_6(l) = P_4O_6(g) \qquad \Delta H = 9{,}400 \text{ cal}$$

Phosphorus trioxide is decomposed by heat, slowly at about 210° and more rapidly at higher temperatures. The reaction is

$$2P_4O_6 = 3P_2O_4 + 2P \text{ (red)}$$

When heated with iodine and carbon disulfide in a closed tube, the reaction that takes place is

$$5P_4O_6 + 8I_2 = 4P_2I_4 + 6P_2O_5$$

With an excess of water P_4O_6 forms two liquid layers which react slowly to form a solution of phosphorous acid, H_3PO_3, and small amounts of phosphoric acid and phosphorus. If a mixture of P_4O_6 and cold water is shaken vigorously, only H_3PO_3 is formed. $P_4O_6 + 6H_2O = 4H_3PO_3$. However, with hot water P_4O_6 reacts vigorously to form P, PH_3, H_3PO_4, and other products [Wolf, Jung, and Tschudnowsky, *Ber.*, **65,** 488 (1932)].

The reaction between P_4O_6(l) and oxygen is slow at room temperatures and, under the proper conditions, produces the green glow discussed in a previous section. The glow has the same spectrum as that observed in the oxidation of white phosphorus by oxygen. Some moisture seems to be essential for the formation of the glow when phosphorus trioxide and oxygen react; the intensity of the glow shows a maximum when the pressure of oxygen is varied slowly from zero to one atmosphere. If dry air at 10–12 mm is passed successively through a bulb containing P_4O_6 on its inner surface, then through slightly damp cotton, and immediately

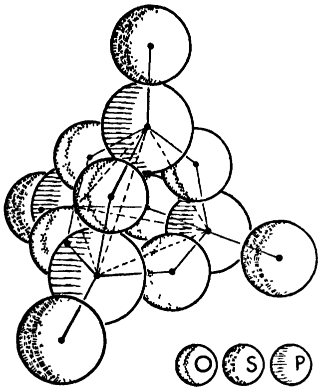


Fig. 34. The Molecular Structures of the $P_4O_6S_4$, P_4O_6, and P_4O_{10} Molecules. $P_4O_6S_4$ is shown. If the four sulfur atoms were omitted, the picture would be that of P_4O_6, and if the four sulfur atoms were oxygen atoms (designated as O′), the picture would be that of P_4O_{10}.

	P—O	P—S	P—O′	P—P	∠O—P—O	∠P—O—P	∠O—P—S	∠O—P—O′
$P_4O_6S_4$	1.61Å	1.85Å	—	2.85Å	101.5°	123.5°	116.5°	—
P_4O_{10}	1 62	—	1.39Å	2 85	101.5	123.5	—	116 5°
P_4O_6	1.65	—	—	2.96	99	127 5	—	—

thereafter through a capillary tube, the green glow appears at the entrance of the capillary [Cristina Miller, *J. Chem. Soc.*, 1823, 1829 (1929); *Proc. Roy. Soc. Edin.*, **46,** 259, 761 (1926)].

The rate of oxygen absorption by liquid phosphorus trioxide [Schenck, Mihr, and Bathien, *Ber.*, **39,** 1506 (1906)] is said to be proportional to the square root of the oxygen pressure, that is, $-dp_{O_2}/dt = k_2 p_{O_2}^{1/2}$; but the absolute value of k_2 depends on the surface of P_4O_6(l) exposed, the rate of its evaporation, and the temperature. In one experiment made at 40.3° with 5 cc of P_4O_6(l) in a 25-cc vessel, the results in the accompanying tabulation were obtained. Owing to the number of variables involved, it is not possible to make definite statements concerning the reaction mechanism. Moreover, if we use the data to evaluate the constant in the first-order rate equation, $-dp_{O_2}/dt = k_1 p_{O_2}$, the values of k_1 are about as constant as those found

t (min)	p_{O_2} (mm)
0	2102
90	2026
240	1902
625	1651

for k_2 defined above. If it can be assumed that the reaction is with the vapor and that this always has its equilibrium pressure, then possible mechanisms corresponding to the two approximate rate laws would be, respectively,

First-order:
$P_4O_6(g) + O_2 = P_4O_8$ (slow)
$P_4O_8 + O_2 = P_4O_{10}$ (rapid)
Half-order:
$O_2 = 2O$ (rapid, reversible)
$P_4O_6 + O = P_4O_7^*$ (slow)
$P_4O_7^* + O$ or $O_2 =$ Products (rapid)

In either case P_4O_{10}, phosphorus pentoxide, is the final product. Although the first mechanism is a more satisfying one chemically, the experimental data are not sufficient to establish it. A complete mechanism would also require the introduction of excited phosphorus monoxide molecules, since the spectrum of the green glow is known to be due to PO.

Phosphorus tetroxide, P_nO_{2n}

This oxide is formed in small amounts when white phosphorus is slowly oxidized by oxygen, but it is best prepared by heating P_4O_6 in a sealed, evacuated tube at 200–250° for two or three days. The resulting red mixture of P (red) and P_nO_{2n} (designated hereafter by P_2O_4) is heated in such a way that the elementary phosphorus is sublimed to one end of the tube and that section then sealed off. On heating the remaining oxide still hotter, the P_2O_4 sublimes free from the small amount of residue and condenses to highly lustrous, transparent crystals that apparently belong to the cubic family [West, *J. Chem. Soc.*, **81,** 923 (1902)]. The vapor density of phosphorus tetroxide at 1400° corresponds to a molecular weight of 459 ± 20; the formula weight of PO_2 is 63, and $\frac{459}{63} = 7.3 \pm 0.3$, a result that leads to the formula P_7O_{14} for the so-called tetroxide. While this formula does not appear unreasonable, it must be noted that some regard a more probable formula to be P_8O_{16}. The vapor density at 500° of a more volatile form of the tetroxide gives a much lower molecular weight, corresponding approximately to the formula P_4O_8 [Emmett and Schultz, *Ind. Eng. Chem.*, **31,** 105 (1939)]. Inasmuch as the molecular formula is not certain, it will be given the purely conventional designation P_2O_4 here; it is clear from the vapor-density measurements that this formula is not correct, but it will serve many of our purposes. The density of the solid is 2.537 at 22.6°.

Phosphorus tetroxide is not affected by heat or light, and it is not soluble in organic solvents. It sublimes on heating, but the vapor pressure of the most stable form becomes one atmosphere only at rather high temperatures; vapor-density determinations were not possible much below 1400°. It dissolves slowly in water with a hissing sound and with the evolution of small amounts of phosphine. The properties of the solutions correspond to those of a mixture of $(HPO_3)_n$ and H_3PO_3, namely, metaphosphoric and phosphorous acids.

Phosphorus pentoxide, P_4O_{10}

Phosphorus pentoxide is the principal product of the complete oxidation of white or red phosphorus. To be sure, the product resulting from the burning of phosphorus in air or oxygen is rarely a single compound, and the conditions can be so controlled that P_4O_6 is formed in the larger quantity, rather than P_4O_{10}; but with excess air or oxygen and under ordinary conditions of burning, the major amount of the oxide formed is phosphorus pentoxide. In the older methods of manufacture of the pentoxide, the phosphorus burns above a container in such a way that the powder-like oxide falls into it. The small-to-moderate amounts of P_4O_6 and P_2O_4 present must be removed by long heating at 175–200° in a current of air or by treatment with ozone.

A method of oxidizing phosphorus vapor which is of practical interest utilizes carbon dioxide as an oxidizing agent. It is found that at about 1000°C an equilibrium is established between phosphorus tetroxide, phosphorus pentoxide, carbon dioxide, and carbon monoxide [Emmett and Schultz, *Ind. Eng. Chem.*, **31**, 105 (1939)]. The equilibrium data could not be readily interpreted, apparently because of the presence of a number of molecular species of the phosphorus oxides. The equation which best fits the data is

$$P_2O_4 + CO_2 = P_2O_5 + CO$$

The values of K experimentally obtained ranged from 0.18 to 0.62 at 1000°C, although it is not at all certain that the flow method used gave equilibrium results. The authors felt that one may safely say that when the ratio of tetravalent phosphorus oxide to pentavalent oxide is one to one, the ratio of carbon dioxide to carbon monoxide will be about two to one. A disadvantage of the method is that a mixture of pentoxide and tetroxide is produced. If, however, quartz or phosphate rock is present, the pentoxide is absorbed and complete oxidation of the phosphorus to the pentavalent state achieved.

Phosphorus pentoxide is not conveniently obtainable by the dehydration of any of the phosphoric acids, $(HPO_3)_n$, $H_4P_2O_7$, and H_3PO_4. Indeed, the outstanding characteristic of phosphorus pentoxide is its ability to absorb water, and at room temperature the vapor pressure of water above a P_4O_{10}-$(HPO_3)_n$ mixture is less than 10^{-5} mm Hg.

The phosphorus pentoxide of commerce is a fairly nonvolatile, white, amorphous powder, but this is only one of the several modifications in which the substance exists. For reasons of difficult experimentation, investigations of the various forms are incomplete. It is known that a finely crystalline, volatile form results when ordinary phosphorus pentoxide is sublimed in a vacuum or in an atmosphere of carbon dioxide. When this finely crystalline form is heated to 400–500°, it is transformed into the ordinary amorphous or powdery form. If the amorphous form is heated to about 570°, it melts and goes over into a glass-like form; the melting point is indefinite. The glass-like form can be caused to crystallize to a second crystalline modification by prolonged heating at 500°; the fine, needlelike crystals of this form melt at 569°. Another crystal-like modification, the third, seems also to exist. The following list gives the designations and methods of preparation of the four well-established forms of $P_4O_{10}(s)$.

α Crystalline, volatile form. Formed by subliming P_4O_{10}.
β Amorphous, powdery form. Formed by heating α at 400–500°.
γ Glassy form. Formed by melting β at about 570°.
δ Crystalline form. Formed as fine needles by prolonged heating of γ at 500°; melting point, 569°.

The α form is by far the most volatile, its vapor pressure being 1 atm at about 358°. The vapor pressures of the β and γ forms are much lower and show no discontinuity during progress from one form to the other. Fig. 35 and the following table present the most recent vapor-pressure measurements of Hoeflake and Scheffer [*Rec. trav. chim.*, **45**, 191 (1926)]. It is not absolutely certain that vapor-solid equilibrium is always obtained in measurements on phosphorus pentoxide; moreover, the vapor pressure at a given temperature depends in some measure on the method of preparation of the form studied [Smits and Rutgers, *J. Chem. Soc.*, **125**, 2573 (1924); Smits and Deinum, *Proc. Acad. Sci. Amsterdam*, **33**, 514 (1930)].

TABLE 48
VAPOR PRESSURES OF PHOSPHORUS PENTOXIDE

The α-Crystalline-modification		The β and γ Amorphous and Glasslike Forms		The δ-Crystalline-modification	
t (°C)	p (cm)	t (°C)	p (cm)	t (°C)	p (cm)
260	3	432	5	501.5	8
280.5	6	476	12	517	13
305.5	14.5	506	20	541	26
330	32.5	541	35.5	563	47
356	66.5	567	54.5		
374	114.5	590	74.5		
401	225.5				

If the α form is heated rapidly in a sealed, evacuated tube, it melts completely to a clear, colorless liquid which, after ten seconds or so, solidifies to a stable modification. The triple point is 423°, with a triple-point pressure of 380 cm of mercury [Smits, *Z. phys. Chem.*, **B 46,** 43, (1940)]. Vapor-pressure measurements, necessarily rough, as only the maximum pressure could be measured, showed the liquid to be entirely distinct from ordinary liquid P_4O_{10}. The vapor-pressure curve fits nicely onto that of the solid α form. Phosphorus pentoxide thus shows the remarkable behavior of having a metastable modification which exists in both the solid and the liquid form.

The nature of the α and δ modifications has been explained to a considerable extent by crystal structure investigations by de Decker and MacGillavry [*Rec. trav. chim.*, **60,** 153 (1941)] and de Decker [*ibid.*, **60,** 413 (1941)]. The α form was obtained as fine needles by sublimation of P_4O_{10} in dry oxygen at room temperature, or as large crystals by sublimation at 400°. Both crystal habits had the same rhombohedral structure. A detailed examination showed that the crystals consisted of distinct P_4O_{10} molecules packed together. The dimensions and configuration of the single molecules were the same as those determined for the gas molecules (their structure is described later in this section). The X-ray density is 2.30 g/cm^3 at room temperature. Crystals of the δ form were prepared by heating the α form in a sealed tube at over 500° for some time. These crystals were orthorhombic and were found to have a structure built up of linked PO_4 tetrahedra. The structure is thus continuous, and there are no single molecules. The detailed determination of the parameters showed that the individual bond distances and angles are closely equal to those of the gas molecule. The X-ray density is 2.72 g/cm^3. These structures reveal clearly the reason for the difference in volatility—only Van der Waals' forces must be overcome to vaporize the α form, but chemical bonds must be ruptured to vaporize the δ form.

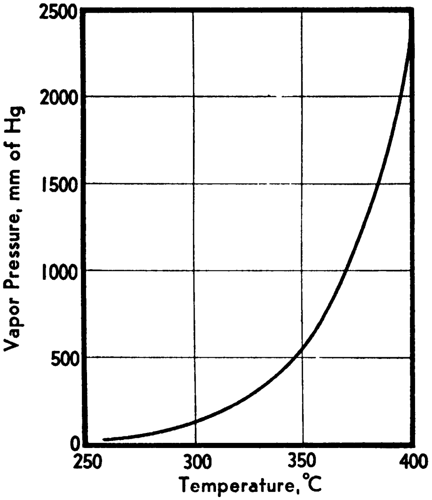


Fig. 35. The Vapor Pressure of α-crystalline Phosphorus Pentoxide, P_4O_{10}.

It is evident that the α form is the least and the δ form the most stable of the known modifications. The α form is metastable at all of the temperatures investigated; the conditions under which it would exist in equilibrium with any of the other established modifications are not known. For thermodynamic purposes, it would be natural to take the δ form as the standard state at room temperatures, but the modification which is most easily prepared and investigated is more commonly chosen for this purpose. In accord with this practice the α form would be selected, although the δ form has preference. No doubt thermodynamic investigations of phosphorus compounds will receive more attention in the future, and a decision on the question of the standard state for $P_4O_{10}(s)$ will be made then.

No reversible reactions have been found whose study would lead to accurate values of the free energy of formation of phosphorus pentoxide. The following thermal data are available [Frandsen, *U. S. Bur. Stds. J. Res.*, **10,** 35 (1933); Bichowsky and Rossini, *Thermochemistry*]:

$$4P(w) + 5O_2(g) = P_4O_{10}(\alpha) \qquad \Delta H^\circ_{291} = -720{,}000 \text{ cal}$$
$$P_4O_{10}(\alpha) = P_4O_{10}(g) \qquad \Delta H^\circ = 17{,}600 \text{ cal}$$
$$P_4O_{10}(\delta) = P_4O_{10}(g) \qquad \Delta H^\circ_{298} = 37{,}750 \text{ cal}, \quad \Delta F^\circ_{298} = 24{,}574 \text{ cal}$$
$$P_4O_{10}(\alpha),\ C_P = 44.34 + 0.1561t - 16.90 \times 10^{-5}t^2 \text{ cal/deg}$$
$$P_4O_{10}(g),\ C_P = 73.6 \text{ cal/deg} \quad (\text{Average for } 358\text{–}1100^\circ)$$

It has long been known that phosphorus pentoxide exists, in the vapor phase, as double molecules, P_4O_{10}, and their structure has been determined recently by means of electron-diffraction studies and is shown in Fig. 34 (p. 177) [Hampson and Stosick, *J. Am. Chem. Soc.*, **60,** 1914 (1938)]. In this compound, the phosphorus bond angle, OPO = 101.5°, is very closely that shown by this element in a number of compounds; namely, PF_3 99°, PCl_3 100°, PBr_3 100°, PI_3 98°, $POCl_3$ 104°, and $P(CH_3)_3$ 100°, the assigned error being around ±2° to 4°.

A notable characteristic of phosphorus pentoxide is the speed and completeness with which it absorbs water. When water is absorbed in small quantities, polymers of metaphosphoric acid, $(HPO_3)_n$, are formed, and further successive additions of water lead to pyrophosphoric acid, $H_4P_2O_7$, and orthophosphoric acid, H_3PO_4, the last being the common form in which phosphoric acid is encountered. The rate at which meta- and pyrophosphoric acids hydrolyze to the ortho acid is not rapid.

The Phosphorus Sulfides

Phosphorus sulfides

The compounds formed by phosphorus and sulfur are not, in general, the analogues of the corresponding oxides of phosphorus. It will be recalled that the well-defined phosphorus oxides are P_4O_6, $(PO_2)_n$, and P_4O_{10}; and, curiously enough, only one of these has its analogue among the known phosphorus sulfides, P_4S_3, P_4S_5, P_4S_7, P_3S_6(?), and P_4S_{10}

The difference between the oxides and sulfides is considerably greater than that encountered between metallic oxides and sulfides, but the difference brings once more to our attention the well-known fact that extrapolations to or from the first row of the periodic system are frequently unreliable. This circumstance, in turn, is to be correlated with the different electronic structures of the atoms in the first row as compared with those of the succeeding rows.

Before describing the properties of the phosphorus sulfides in detail, it will be helpful to summarize some of the known facts by means of a table showing the important physical constants [see Stock and Herscovici, *Ber.*, **43**, 415, 1223 (1910)]. It will be noted at once that the minima or maxima in the physical constants are found with P_4S_7.

TABLE 49
PHYSICAL PROPERTIES OF THE PHOSPHORUS SULFIDES

	P_4S_3	P_4S_5	P_4S_7	P_4S_{10}
Color:				
Solid.	Yellow	Sulfur yellow	Almost white	Yellow
Liquid.	Brownish yellow	—	Light yellow	Reddish brown
Density of solid at 17°.	2 03	2.17 (25°)	2.19	2 09
Melting point (°C)	171–172.5	170–220	305–310	286–290
Boiling point (°C).....	407–408	—	523	513–515
Solubility (g/100 g solvent):				
CS_2 17°.........	100	≈10	0.029	0.222
0°.........	27.0	—	.005	.182
−20°.........	11.1	—	—	.0833
C_6H_6 17°.........	2.5	—	—	—
80°.........	11.1	—	—	—
Action with cold water	Scarcely attacked		Fairly readily decomposed	Slowly decomposed
Stability of solid on standing in air.	Scarcely decomposed		Decomposes	Slowly decomposed

Tetraphosphorus trisulfide, P_4S_3

This compound is formed by heating a mixture of red phosphorus and powdered sulfur {4P (+ excess) + 3S} in a glass tube gradually to 100° and then more strongly, especially near the surface of the mixture, until the reaction starts and spreads through the mixture. The preparation should be carried out in an atmosphere of CO_2 or in an evacuated tube to avoid any oxidation by the air. Following the reaction, the mixture should be heated strongly until distillation begins, in order that a minimum of higher sulfides be present. After cooling, the mass is extracted with CS_2 or it is distilled in an atmosphere of CO_2. The final product, after recrystallization, is yellow in color and the rhombic crystals are readily soluble in CS_2, C_6H_6, and toluene (31.2g at 17° and 15.4g at 111° dissolve in 100g of toluene). [See, for example, Stock and Von Bezold, *Ber.*, **41,** 657 (1908); Stock and Rudolph, *Ber.*, **42,** 2062 (1909); **43,** 150 (1910).] An impure form is made commercially by simply heating red phosphorus and powdered sulfur in the proper proportions (S in excess) at 330° in an atmosphere of CO_2. This product is used in the manufacture of certain types of matches.

The molecular weight of P_4S_3 has been determined in boiling benzene and for the vapor alone. In benzene solution, the molecular weight is found to be from 228 to 264, the formula weight of P_4S_3 being 220. Measurements of the vapor density lead to the molecular weights shown in the tabulation [Stock and Von Bezold, *Ber.*, **41,** 657 (1908)]. The decrease in the calculated molecular weight with increasing temperature indicates the decomposition of P_4S_3 into phosphorus and sulfur vapors; if account were taken of the nature of the molecular species of the two latter substances, equilibrium constants for the reversible decomposition reaction could, in principle, be calculated. Because the precision claimed for the vapor-density measurements is not high, the evaluation of any equilibrium constants is hardly worth while. The experimental vapor densities are of value, however, in showing that at 750° and lower the vapor molecules are P_4S_3, and that, further, the reversible decomposition reaction at higher temperatures could be employed for the determination of the free energy of the compound.

Temp. (°C)	Molecular Weight, P_4S_3
700	219
750	213
800	202
850	185
900	182
950	179
1000	179

When heated in oxygen, P_4S_3 luminesces in a manner that recalls P(w) and P_4O_6. In experiments made at 70° in an atmosphere of dry oxygen, it was observed that when $p_{O_2} = 386.75$ mm, an intermittent greenish glow appears about the solid P_4S_3. As the pressure was decreased, the glow finally became steady at $P_{O_2} = 321.85$ mm. The pressure of oxygen was then increased slowly and the intermittent effect appeared again; but at $P_{O_2} = 389.25$ mm, the glow stopped altogether [Scharff, thesis, Marburg, 1907; Mellor, *Comprehensive Treatise*]. Corresponding experiments at other temperatures show the same effect, if the temperatures are not too low.

P_4S_3 is only gradually decomposed by boiling water, and cold hydrochloric and sulfuric acids have scarcely any action on it at all (Lemoine). With cold nitric acid, elementary sulfur and phosphorus oxyacids are formed, and cold *aqua regia* is capable of oxidizing and dissolving the solid P_4S_3 completely to form phosphoric and sulfuric acids. When finely divided, P_4S_3 reacts rapidly with solutions of potassium hydroxide to form sulfide ion, phosphine, hydrogen, hypophosphite, and phosphite.

Liquid ammonia dissolves P_4S_3 to form a reddish-brown solution which becomes dark red with time and finally is transformed into a brown jelly. After evaporation of the ammonia and the phosphine that results from the reaction, a viscid mass containing thiophosphates and other substances remains. Both ether and alcohol dissolve P_4S_3 with decomposition.

Tetraphosphorus trisulfide undergoes a number of interesting reactions in carbon bisulfide solution. With iodine, each P_4S_3 consumes about eight equivalents of the halogen, and this result is explained by two reactions

$$7P_4S_3 \text{ (in } CS_2) + 24I_2 \text{ (in } CS_2) = 16PI_3 \text{ (in } CS_2) + 3P_4S_7$$
$$P_4S_3 + 4I_2 = P_4S_3I_8$$

since the yield of P_4S_7 is only some 34%. It is known that P_4S_7 and P_4S_{10} are not oxidized by iodine in carbon bisulfide solution. Over eight (8.3) equivalents of bromine are consumed per mole of P_4S_3 in CS_2 solution, and the products of the reaction appear to be mainly PB_3 and P_4S_{10} [Treadwell and Beeli, *Helv. Chim. Acta*, **18,** 1161 (1935)].

$$10P_4S_3 \text{ (in } CS_2) + 42Br_2 \text{ (in } CS_2) = 28PBr_3 \text{ (in } CS_2) + 3P_4S_{10} \text{ (in } CS_2)$$

The yellow crystalline compound $P_4S_3I_2$ is stated to result from a reaction between P_4S_3 and I_2 in CS_2 solution.

Solutions of P_4S_3 and sulfur in carbon bisulfide react slowly in the presence of light to give phosphorus sulfides that are not obtainable by heating phosphorus and sulfur together. Thus, Dervin [*Compt. rend.*, **138,** 366 (1904)] reports pale-yellow needles of P_3S_6 as well as crystalline spherical grains of P_8S_{11} as resulting from the photochemical reaction. By allowing the mixture 11 g P_4S_3 + 3.5 g S + 0.1 g I_2 in 100 cc CS_2 to stand in diffuse daylight for three days, Treadwell and Beeli [*Helv. chim. Acta*, **18,** 1161 (1935)] obtained over 11 g of sulfur-yellow crystals whose composition and molecular weight in boiling CS_2 correspond to P_4S_5. Of the less common phosphorus sulfides, P_4S_5 has been best established.

Solid mixtures of P_4S_3 and P_4S_{10}, when heated in vacuum at 90–95° for some 25 hours, yield a sublimate of the former compound only and a residue consisting principally of P_4S_{10}. The two compounds may, therefore, be separated by vacuum distillation. P_4S_3 and P_4S_7 may be separated in the same way, the residue in this case having a composition corresponding, perhaps accidentally, to P_4S_5. Sulfur alone sublimes first from P_4S_3—S mixtures at 90–95° in vacuum. The wide difference in solubility of the phosphorus sulfides in carbon bisulfide and benzene is most conveniently employed to separate and purify the substances [Beeli, *Helv. Chim. Acta,* **18,** 1172 (1935)].

White phosphorus, when molten, will dissolve much sulfur, but no compound is formed between the two elements unless the mixtures are strongly heated.

Tetraphosphorus pentasulfide, P_4S_5

This compound is formed when a solution of P_4S_3 (11 g), sulfur (3.5 g), and iodine (0.1 g) in carbon bisulfide (100 cc) is exposed to diffuse daylight for three days. It results also when a molten mixture of 2P (red) + 3S is slowly cooled. One of the principal reaction products is P_4S_7, but it is left for the most part unextracted by boiling carbon bisulfide, in which P_4S_5 is moderately soluble. The composition of the slowly cooled phosphorus-sulfur melt indicates an equilibrium reaction [Treadwell and Beeli, *Helv. Chim. Acta,* **18,** 1161 (1935)]:

$$2P_4S_5 = P_4S_3 + P_4S_7 \quad \text{(Reversible)}$$

In boiling carbon bisulfide, P_4S_5 shows a molecular weight of 294–342, the formula weight being 284.4. The crystals of the substance are sulfur yellow in color, and they melt in the range 170–220° to give a sticky, slowly solidifying mass [Treadwell and Beeli, *loc. cit.*].

Tetraphosphorus heptasulfide, P_4S_7

When a mixture of red phosphorus and sulfur in the proportions 2P + 3S is melted in a glass tube, or when 4P + 7S + 5% P_4S_3 are heated in a hard glass tube until distillation becomes evident, the compound P_4S_7 is formed along with small amounts of the other sulfides. The more soluble P_4S_3 and P_4S_{10} may be extracted with carbon bisulfide, and the resulting residue of P_4S_7 may be purified by recrystallization from the same solvent. The compound is also formed by heating a carbon bisulfide solution of $P_4S_3 + P_4S_{10}$ at 100° [Stock and Rudolph, *Ber.*, **42,** 2062 (1909); *Ber.*, **43,** 150 (1910); Stock and Herscovici, *Ber.*, **43,** 415, 1223 (1910)]. The purified compound is nearly colorless or pale yellow; it melts at 305–310°, and it boils at 523°. It is the least soluble of all the phosphorus sulfides in carbon bisulfide. Vapor-density measurements by Stock and Herscovici yielded the accompanying molecular weights for the gas. These results exhibit two things of interest, namely, that at the lowest temperatures the vapor consists of P_4S_7 molecules, and at the highest temperatures the observed molecular weights are very nearly equal to one-half of the formula weight. This fact might suggest immediately

Temp. (°C)	Molecular Weight
700	337
750	323
800	202
850	193
900	179
950	173
1000	167

Formula weight, P_4S_7 = 348.

that P_4S_7 dissociates into two simple molecules, but it is not at all certain that this is the case. For example, if the dissociation proceeds reversibly according to the equation $P_4S_7(g) = P_4S_3(g) + \frac{2}{3}S_6$, and if account is taken of the assumed reaction $P_4S_3(g) = P_4(g) + \frac{1}{2}S_6(g)$ and the known equilibria $P_4(g) = 2P_2(g)$ and $S_6(g) = 3S_2(g)$, then at some temperature the observed molecular weight of the vapor will equal one-half the formula weight. It is, of course, possible that the decomposition is more complicated still and in such a way that the less-known phosphorus sulfides, P_4S_5, P_2S_6, and so on, are also present in the vapor. It would be of interest to make an accurate study of both $P_4S_3(g)$ and $P_4S_7(g)$ with respect to their reversible decomposition at higher temperatures.

Tetraphosphorus heptasulfide is much more reactive with moisture than the other phosphorus sulfides. This reactivity suggests that P_4S_7 rather than the more commonly used P_4S_{10} might be the more effective reagent to use in organic reactions in which sulfur is to be substituted in certain classes of carbon compounds.

Triphosphorus hexasulfide, P_3S_6 (?)

There is some uncertainty regarding the existence of this compound. It is said to be formed when the molten mixture P (red) + 2S is distilled or when the same proportions of phosphorus and sulfur are heated to melting [Mai, *Ann.*, **265**, 192 (1891); Von Bezold, thesis, Berlin, (1908)]. Vapor-density measurements lead to a molecular weight corresponding approximately to P_4S_8, but the boiling-point elevations of carbon bisulfide solutions are in accord with the formula P_3S_6. The compound is said to exist as pale-yellow, needle-like crystals which melt at 296–298° and boil at 516–519°. These values correspond closely to those shown in the table for P_4S_7. The vapor of the substance at 340° and 11 mm pressure is pale green in color.

Phosphorus pentasulfide, P_4S_{10}

The name of this well-known sulfide, like that of the corresponding oxide, was assigned and came into general use before the doubled molecular weight was established. Its preparation is quite similar to that of the other phosphorus sulfides and consists of heating a mixture of powdered red phosphorus and sulfur in the proportions 2P(red) + 5S (+10% excess) in an atmosphere of carbon dioxide until reaction begins [Stock and Scharfenberg, *Ber.*, **41**, 558 (1908)]. A better preparation is obtained if a reacted mixture whose initial composition was 2P (red) + 5S (+1% excess) is heated in a closed, previously evacuated glass tube at 700°. The pressure in the heated tube may amount to several atmospheres [Stock and Herscovici, *Ber.*, **43**, 1223 (1910)].

In either method of preparation, the cooled solid is extracted with carbon bisulfide, a solvent in which the pentasulfide is somewhat soluble

Repeated recrystallizations from hot carbon bisulfide solution results in beautiful, pale-yellow crystals which melt to a red-brown liquid at 286–290°. The colored liquid boils at 513–515°, and, if the vapor is condensed rapidly, a white, more reactive form of the pentasulfide results.

The following vapor-density measurements show that $P_4S_{10}(g)$ is extensively decomposed even at 600° [Stock and Scharfenberg; Stock and Von Bezold, *Ber.*, **41,** 657 (1908)]:

Temp. (°C)	Molecular Weight	Temp. (°C)	Molecular Weight
600	208	800	144
650	196	850	141
670	198	900	136
700	185	1000	133
750	161		

Formula weight, P_4S_{10} = 444.

It is evident, indeed, that at the temperatures investigated little if any of the vapor consists of P_4S_{10} molecules, but it would not be safe to conclude that the vapor molecules consist of P_2S_5, notwithstanding the fact that at the lowest temperatures the molecular weights appear to be approaching 222. It is more likely, in view of the strong tendency for phosphorus sulfides and oxides to contain four atoms of phosphorus, that the vapors of the pentasulfide consist of an equilibrium mixture of the lower sulfides and sulfur. The nature of the equilibrium mixture of the decomposition products is probably worth investigating, but an analysis based on the only moderately accurate vapor-density results cited would not be very significant.

In boiling carbon bisulfide solution, the observed molecular weights of P_4S_{10} vary from 449 to 491, which shows that the doubled formula is correct for the solutions and that doubtless the crystals also do not contain fundamental groups with a smaller number of atoms than does P_4S_{10} [see Stock and Thiel, *Ber.*, **38,** 2720 (1905)]. The solubility of P_4S_{10} in carbon bisulfide is shown in Table 49.

Phosphorus pentasulfide hydrolyzes slowly with cold water and cold alkali, but more rapidly with hot water or hot alkali, to give mainly hydrogen sulfide and orthophosphoric acid together with other products that are set forth in more detail in Table 49.

$$P_4S_{10} + 16H_2O = 4H_3PO_4 + 10H_2S$$

When P_4S_{10} is heated with BiF_3 or PbF_2, the volatile sulfofluoride PSF_3 is formed.

Inasmuch as no thermodynamic studies of the phosphorus sulfides have been made, one has to be content with qualitative notions of their stabilities, and these notions must depend for the most part on the results of vapor-density measurements. From these it is clear that the least stable sulfide is P_4S_{10}, since it is extensively decomposed at 600°, while P_4S_3 is the most stable, since it does not begin to decompose until heated to about 750°. The stability of P_4S_7 is intermediate, but the facts are not so clear in the case of P_4S_5. A further qualitative estimate of the stabilities of the better-known sulfides may be gained from the following approximate heats of reaction [Treadwell and Beeli, *Helv. Chim. Acta,* **18,** 1161 (1935)]:

$$4P\ (\text{red}) + 3S(s) = P_4S_3(s) + 29{,}400\ \text{cal}$$
$$P_4S_3(s) + 4S(s) = P_4S_7(s) + 36{,}300\ \text{cal}$$
$$P_4S_7(s) + 3S(s) = P_4S_{10}(s) + \approx \text{none cal}$$

Hydrolysis of phosphorus sulfides

In the previous sections a detailed account has not been given of the products of the reactions between the phosphorus sulfides and water. This account was postponed so that the results for all of the compounds might be assembled in one place and thus provide the reader with a clear picture of the facts. The results to be given are due to Treadwell and Beeli [*Helv. Chim. Acta,* **18,** 1161 (1935)]; the table shows the percentages of the total phosphorus or sulfur which was recovered as the reaction product listed.

TABLE 50
THE HYDROLYSIS OF THE PHOSPHORUS SULFIDES

Product	Per Cent Recovered in Alkaline Solution*			Per Cent Recovered in Acid Solution		
	P_4S_3	P_4S_7	P_4S_{10}	P_4S_3	P_4S_7	P_4S_{10}
H_2S	94.2	90.0	90 0		90.0	78.0
PH_3	5 0	2.5	—†		2.5	—
H_3PO_2	15.0	1.5	10.0		1.0	10.0
H_3PO_3	75.0	37.5	—		40.0	0.0
H_3PO_4	0.0	57.4	80.0		60.0	85 0
H_2	0 4‡	—	—			

* Following the alkaline hydrolysis, the solutions were acidified before the analyses were made.

† In some cases no analysis was made for the product listed.

‡ Expressed in moles per mole P_4S_3.

It is noteworthy that even in the case of P_4S_{10} appreciable amounts of hypophosphorous acid are formed, thus showing that the compound is unstable and decomposes in the act of hydrolysis into a lower sulfide and sulfur.

Phosphorus sulfoxide, $P_4O_6S_4$

If a mixture of phosphorus trioxide, P_4O_6, and sulfur in the proportions $P_4O_6 + 4S$ is heated gradually in an atmosphere of nitrogen or carbon dioxide, the two substances melt at first to form two liquid layers of which the lower is sulfur, but at about 160° a violent and quantitative reaction occurs to form $P_4O_6S_4$. The preparation of the compound is best carried out by carefully heating from three to five grams of freshly distilled P_4O_6 with the calculated amount of sulfur in a sealed tube containing an atmosphere of nitrogen. When the temperature reaches 154–168°, an almost violent reaction sets in that is complete in two or three seconds. If greater amounts of P_4O_6 and sulfur are used, the violence of the reaction may result in an explosion which is accompanied by an intensely bright flame. In the normal case, the reaction product consists of colorless feathery crystals and a yellowish-gray mass. When sublimed at about 140–150° in a vacuum the sublimate is colorless, but ordinary distillation yields a pale-yellow product [Thorpe and Tutton, *J. Chem. Soc.*, **59,** 1023 (1891)].

Phosphorus sulfoxide melts at about 102° to a viscous liquid which boils at 295°. Vapor-density measurements on the sublimed crystals at 350–400° show the molecular weight to be 343; the formula weight, 348, is within the experimental error equal to this. The vapor-density measurements show also that the compound does not decompose or dissociate at 400° or lower; this is also shown by the fact that the boiling point of the liquid does not change with time or with the amount distilled off.

The crystals of $P_4O_6S_4$ are tetragonal and are readily soluble in carbon bisulfide. They are also soluble in benzene, but solution is accompanied by a reaction that forms dark-colored organic products. Phosphorus sulfoxide deliquesces readily in air and is rapidly dissolved and hydrolyzed by water, the reaction being

$$P_4O_6S_4 + 6H_2O = 4HPO_3 + 4H_2S$$

The metaphosphoric acid formed is doubtless not the monomer, but the actual form is not known.

Phosphorus sulfoxide resembles, in its formula, its stability toward heat, and its reactivity toward water, more the pentoxide than the pentasulfide. The structure of the vapor molecules has been determined by the electron-diffraction method [Stosick, *J. Am. Chem. Soc.*, **61,** 1130 (1939)] and was found, as is shown by Fig. 34, to be similar to that for P_4O_{10}.

CHAPTER 6

The Oxyacids of Phosphorus

The well-established oxyacids of phosphorus are presented in the following list together with the name and a brief statement describing how each acid or one of its salts is prepared.

H_3PO_2	Hypophosphorous Acid	P + hot $Ba(OH)_2$ soln.
H_3PO_3	Phosphorous Acid	$PCl_3(g) + H_2O(l)$
$H_4P_2O_6$	Hypophosphoric Acid	P(w) + O_2 (moist); P (red) + NaClO
$(HPO_3)_n$	Metaphosphoric Acid	From H_3PO_4 heated to fuming. P_2O_5 + little water.
H_3PO_4	Orthophosphoric Acid	P_2O_5 + water; P(w) + HNO_3
$H_4P_2O_7$	Pyrophosphoric Acid	Heat Na_2HPO_4

Only the phosphorous and phosphoric acids can be said to possess acid anhydrides, namely, P_4O_6 and P_4O_{10}, respectively. Phosphorus tetroxide P_2O_4 might be formally regarded as the anhydride of hypophosphoric acid, but it does not combine with water to form hypophosphoric acid; a mixture of phosphorous and phosphoric acids results instead.

Hypophosphorous acid

This acid is prepared by an indirect method. A mixture of one part of white phosphorus, three parts of $Ba(OH)_2$, and water is heated to boiling for a few hours until all of the phosphorus has dissolved. The reaction is:

$$4P(w) + 3OH^- + 3H_2O = PH_3 + 3H_2PO_2^-$$

and since PH_3 is a spontaneously inflammable gas, it is evolved and immediately burned, leaving only the hypophosphite in solution. Excess barium in the solution is precipitated as $BaCO_3$ by treatment with CO_2. After filtering, the solution is evaporated until crystals of barium hypophosphite $Ba(H_2PO_2)_2{\cdot}H_2O$ separate, and these are then dissolved in water (285 g in 5 l water). The resulting solution is treated with an equivalent amount of sulfuric acid, the barium sulfate precipitate is filtered off, and the filtrate is concentrated by evaporation, care being taken that the temperature at no time exceeds 130°. On cooling the concentrate to a few degrees below 0°, colorless crystals of H_3PO_2 separate out in a pure or very nearly pure form, only a small amount, if any, of phosphorous or phosphoric acid being present [Thomsen, *Ber.*, **7,** 994 (1845); for modifications of Thomsen's method, see Marie, *Compt. rend.*, **138,** 1216 (1904)]. Solutions of hypophosphorous acid are quite stable at room temperature and may be purchased in the market.

Crystals of hypophosphorous acid, H_3PO_2, melt at about 26.5°, they are very soluble in water, and, indeed, when exposed to the air, they will deliquesce. The solutions are not oxidized by atmospheric oxygen, but they do act as strong, though sometimes slowly reacting, reducing agents. Characteristic reduction reactions are those with silver nitrate to give black, metallic silver, and with cupric salts to give cuprous salts and metallic copper. Although the solutions of hypophosphorous acid are stable at room temperature, they will decompose if heated to about 140° or above; crystals of H_3PO_2, as well as its salts, also decompose on heating, the decomposition products being principally phosphine, phosphoric acid, and some hydrogen. The formation of hydrogen is most noticeable in alkaline solution at around 100°; hydrogen is also formed in neutral solutions in the presence of catalysts such as palladium or finely divided copper, the former being the more effective catalyst. The rate of the decomposition reaction in alkaline solution at 91° and 100° has been studied by Sieverts and Loessner [*Z. anorg. Chem.*, **76,** 10 (1912)]; the reaction is

$$H_2PO_2^- + OH^- = HPO_3^= + H_2$$

and for a given concentration of hydroxyl ion

$$-\frac{d(H_2PO_2^-)}{dt} = k(H_2PO_2^-)$$

The values of k depend strongly on the (OH^-), as the results in the accompanying tabulation for 100° show. The values of $k/(OH^-)^2$, while not strictly constant, do not vary more than would be expected for solutions of such varying ionic strengths. The complete rate equation therefore appears to have the form:

Conc. NaOH (moles/l)	$k \times 10^4$ (min^{-1})	$[k/(OH^-)^2] \times 10^4$
1.23	4.1	2.71
1.28	5.3	3.23
1.84	9.7	2.87
2.43	15.2	2.57
3.94	51.6	3.33
4.90	98.3	4.09

$$-\frac{d(H_2PO_2^-)}{dt} = k_3(H_2PO_2^-)(OH^-)^2$$

which suggests that the hydrogen liberated does not come from either of the hydrogens bound to phosphorus (see below), but rather from the OH^-. That is,

$$H_2PO_2^- + 2OH^- = H_2PO_3^- + O^= + H_2 \qquad \text{(slow)}$$
$$O^= + H_2O = 2OH^- \qquad \text{(rapid)}$$

The reaction deserves further investigation.

Hypophosphorous acid is a moderately strong monobasic acid, only one hydrogen being available for neutralization. It is for this reason that the formula is sometimes written H_2POOH, it being supposed that the first two hydrogens are attached directly to the phosphorus atom. The correctness of this assumption has been proved by an X-ray study of $NH_4H_2PO_2$ [Zachariasen and Mooney, *J. Chem. Phys.*, **2,** 34 (1934)] and by the Raman spectrum of H_3PO_2 [Simon and Fehér, *Z. anorg. Chem.*, **230,** 289 (1937)]. The ionization constant varies with the concentration of the acid, as the results in the table, due to Kolthoff, show [Kolthoff, *Rec. trav. chim.*, **46,** 350 (1927)]. From these data it is seen that the acid is moderately strong, the degree of ionization being 0.55 at 0.5 m. It is of interest at this point to compare the first ionization constants, K_1, for dilute solutions of the three more common oxyacids of phosphorus, namely, hypophosphorous, phosphorous, and orthophosphoric. Unlike other series of acids (H_2SO_3, H_2SO_4, for example), the first ionization constants vary but little.

$$\frac{(H^+)(H_2PO_2^-)}{(H_3PO_2)} = K$$

Conc. (moles/l)	$K \times 10^2$ at 18°
0.05	6.2
.01	4.0
.005	2.9
.0025	2.0
.001	1.0

Oxyacid	K_1
H_3PO_2	1.0×10^{-2}
H_3PO_3	1.6×10^{-2}
H_3PO_4	0.8×10^{-2}

The alkali and alkaline earth salts of hypophosphorous acid are all quite soluble in water, as are also most of those of the heavier metals. The sodium salt, $NaH_2PO_2 \cdot 5H_2O$, has been used in medicine. Barium hypophosphite, $Ba(H_2PO_2)_2 \cdot H_2O$, is soluble in water to the extent of about 30 g per 100 g of water at ordinary temperatures, and is less soluble in alcohol. The oxidation potential for the half-cell reaction $H_3PO_2 + H_2O = H_3PO_3 + 2H^+ + 2E^-$ is estimated to be 0.59 volts, that is, it lies above hydrogen and between Fe, Fe^{++} and Zn, Zn^{++} (Latimer, *Oxidation Potentials*). Although H_3PO_2 and its salts are powerful reducing agents, they may be reduced to phosphine by the stronger reducing agent zinc.

It has already been pointed out that aqueous hypophosphorous acid, while a very strong reducing agent, is often slow to react with oxidizing agents. This fact is exemplified by the reactions with the halogens and with mercuric and cupric chlorides, all of which proceed at measurable rates. The reaction with iodine [Mitchell, *J. Chem. Soc.*, **117,** 1322 (1920)] and those with bromine and chlorine [Griffith and McKeown, *Trans. Faraday Soc.*, **30**, 530 (1934)] have been carefully investigated, and the results are of sufficient importance to warrant a somewhat detailed consideration. The first, main reaction is

$$H_3PO_2 + X_2 + H_2O = H_3PO_3 + 2H^+ + 2X^-$$

the subsequent reaction,

$$H_3PO_3 + X_2 + H_2O = H_3PO_4 + 2HX$$

being very slow, in acid solution when X_2 is iodine, and measurably rapid with Br_2 and Cl_2 only at low acid concentrations.

It is found that the same mechanism applies to all three of the halogen reactions; consequently the one with bromine will be selected as a representative of the group.

$$\begin{array}{lrcll}
k_1 & H_2PO_2^- + Br_2 \text{ or } Br_3^- + H_2O & = & H_3PO_3 + H^+ + 2Br^- & \\
 & & & & \text{(slow)} \\
 & H_2PO_2^- + H^+ & = & (H_3PO_2)_{\text{I}} & \text{(rapid, reversible)} \\
k' & (H_3PO_2)_{\text{I}} & = & (H_3PO_2)_{\text{II}} & \text{(slow)} \\
k'' & (H_3PO_2)_{\text{II}} & = & (H_3PO_2)_{\text{I}} & \text{(moderately rapid)} \\
k_2 & (H_3PO_2)_{\text{II}} + Br_2 \text{ or } Br_3^- + H_2O & = & H_3PO_3 + 2H^+ + 2Br^- & \\
 & & & & \text{(rapid)}
\end{array}$$

With iodine the first step is so slow that $k_1 \approx 0$. This mechanism is in accord with the following experimentally determined rate equation in which the measured rate constants k_1, k_2, and so forth, are dependent on the concentrations of Br^-, H^+, and other reactants.

$$-\frac{d(\Sigma H_3PO_2)}{dt} = (\Sigma H_3PO_2)(\Sigma Br_2)\left\{k_1\alpha + \frac{k_2k'(1-\alpha)}{k'' + k_2(\Sigma Br_2)}\right\}$$

$$k_{obs} = k_1\alpha + \frac{k_2k'(1-\alpha)}{k'' + k_2(\Sigma Br_2)}$$

where α is the degree of ionization of H_3PO_2. At low acid concentrations (10^{-3} to 10^{-9} m), $\alpha \approx 1$, and the second term in brackets is negligible; under these conditions it is found that k_1 is proportional to

$$\frac{1}{K_3 + (Br^-)}$$

where

$$K_3 = \frac{(Br_2)(Br^-)}{(Br_3^-)}$$

From this dependence of k_1 on (Br^-) it follows that $H_2PO_2^-$ reacts with Br_2 and not with Br_3^- or HBrO, because $\Sigma Br_2 = (Br_2) + (Br_3^-)$ and

$$\frac{(Br_2) + (Br_3^-)}{K_3 + (Br^-)} = \frac{(Br_2) + (1/K_3)(Br_2)(Br_3^-)}{K_3 + (Br^-)} = \frac{(Br_2)}{K_3}$$

Hence, when $\alpha \approx 1$

$$-\frac{d\Sigma H_3PO_2}{dt} = \frac{k_1}{K_3}(\Sigma H_3PO_2)(Br_2)$$

When $(Br^-) = 1.137$, $k_1 = 3.9$ at 10° and 0.975 at 0.25°, with concentrations expressed in moles/liter and the time in minutes. At high acid concentrations, $k_1\alpha$ becomes small compared with the term in k_{obs} having the factor $(1 - \alpha)$.

The most interesting feature of the mechanism is the assumption of two forms of H_3PO_2, with a slow, reversible reaction involved when one form goes over into the other. Mitchell renders these two forms more specific by assuming the reaction

$$H_3PO_2 + H_2O = H_5PO_3 \qquad \text{(slow, reversible)}$$

k' is found to be directly proportional to (H^+), and at 10° and $(H^+) = 1$ it has the value 0.041. If the reactivity of $(H_3PO_2)_{II}$ is greater than that of $(H_3PO_2)_I$ with other oxidizing agents, the values of k' should be equal and independent of the oxidizing agent. That this is the case is shown by the fact that at 25°, $k' = 0.21$, which is effectively equal to the value 0.256 found in the iodine reaction at the same temperature.

The catalytic effect of H^+ on the reaction between the two forms of H_3PO_2 recalls that attending several hydrolytic reactions, and it suggests that H_3O^+ is the carrier of the water. Accordingly, we may replace Mitchell's reaction by

$$\begin{aligned} H_3PO_2 + H_3O^+ &= H_5PO_3 + H^+ \qquad &\text{(slow)} \\ H^+ + H_2O &= H_3O^+ \qquad &\text{(rapid)} \end{aligned}$$

It is not possible to evaluate k'' and k_2 separately; only the ratio k''/k_2 appears in the rate equation. When the acid concentration is high, the term $k_1\alpha$ in brackets in

$$k_{obs} = \left\{k_1\alpha + \frac{k_2k'(1 - \alpha)}{k'' + k_2(\Sigma Br_2)}\right\}$$

is small compared to the second term. Thus with $(HBr) = 1.137$ and $(\Sigma Br_2) = 0.0025$, $k_1\alpha = 0.3$, while $k_{obs} = 4.36$. In experiments with added $(H_2SO_4) = 2.92$ m and $(\Sigma Br_2) = 0.002$ m, k_{obs} varied but little with (Br^-) ($k_{obs} = 3.2$ at 0.5 n and 4.2 at 0.025 n Br^-), and consequently the reactant with $(H_3PO_2)_{II}$ appears to be both Br_2 and Br_3^-, since the second term in brackets, and hence k_2, does not vary with (Br^-). HBrO is not the reactant, since the ratio k''/k_2 is found to be directly and not inversely proportional to the acid concentration.

For $(H^+) = 1$, k''/k_2 was found to be of the same order of magnitude for all three of the halogen reactions.

Reaction	Temp. (°C)	k''/k_2
I_2	25	$\frac{1}{80}$
Br_2	10	$\frac{1}{140}$
Br_2	0	$\frac{1}{150}$
Cl_2	0	$\frac{1}{120}$

Since k''/k_2 is independent of the halogen acting as oxidizing agent, and since, moreover, its temperature dependence was found to be small, it may be assumed that $(H_3PO_2)_{II} + X_2 + X_3^-$ takes place at every collision; that is, $k_2 \approx 4 \times 10^{12}$, and hence $k'' \approx 3 \times 10^{10}$. This assumption permits the evaluation of the equilibrium constant

$$K = \frac{(H_3PO_3)_{II}}{(H_3PO_2)_I} = \frac{k'}{k''} \approx 10^{-12}$$

In arriving at these values, it is assumed further that the dependence of k''/k_2 on (H^+) implies the dependence of k'' but not of k_2 on (H^+), and this seems reasonable in view of the catalytic effect of H^+ on the reaction $(H_3PO_2)_I = (H_3PO_2)_{II}$.

We may summarize the results of the study of the hypophosphorous acid-halogen reactions in terms of the following more specific mechanism:

$$\begin{array}{lrcll}
k_1 & H_2PO_2^- + X_2 + H_2O & = & H_3PO_3 + H^+ + 2X^- & \text{(slow)} \\
 & H_2PO_2^- + H^+ & = & H_3PO_2 & \text{(rapid, reversible)} \\
k' & H_3PO_2 + H_3O^+ & = & H_5PO_2 + H^+ & \text{(slow)} \\
k'' & H_5PO_2 + H^+ & = & H_3PO_2 + H_3O^+ & \text{(moderately rapid)} \\
k_2 & H_5PO_2 + X_2 \text{ and } X_3^- & = & H_3PO_3 + 2H^+ + 2X^- + H_2O &
\end{array}$$

The chlorine reaction is more rapid than the bromine reaction; the values of k_{obs} at 0.2° and (HCl) = 1.012 n vary from 2.82 to 4.46, while the corresponding quantity in the bromine reaction varies, for (HBr) = 1.137 n, from 0.305 to 1.706. The iodine reaction is the slowest of the three under the same conditions of concentration and temperature.

It is a striking fact that the reduction of $HgCl_2$ and $CuCl_2$ in acid solution is also in accord with a mechanism involving the slow reversible reaction $(H_3PO_2)_I = (H_3PO_2)_{II}$. These two reactions and the iodine reaction differ from the bromine and chlorine reactions in that in the former the rate of oxidation of $(H_3PO_2)_I$ or $H_2PO_2^-$ is too small to be measurable. Accordingly, the rate-determining step for moderate concentrations of oxidizing agent will be

$$(H_3PO_2)_I = (H_3PO_2)_{II}$$

or better,

$$H_3PO_2 + H_3O^+ \underset{k''}{\overset{k'}{\rightleftharpoons}} H_5PO_3 + H^+$$

followed by the moderately rapid reaction

$$H_5PO_3 + I_3 \overset{k_2}{=} H_3PO_3 + 2H^+ + 3I^-$$

At very low concentrations of I_3^-, $CuCl_2$, or $HgCl_2$, the rate of the second reaction becomes small, and the rate of reduction of the oxidizing agent is no longer governed mainly by the rate at which $(H_3PO_2)_I$ goes over into $(H_3PO_2)_{II}$. But when the concentrations of I_2^-, $CuCl_2$, or $HgCl_2$ are moderate or large,

$$-\frac{d(H_3PO_2)}{dt} = k(H_3PO_2)(H^+)$$

That is, the rate is practically independent of the concentration of oxidizing agent. The following values of k for the three oxidizing agents I_2^-, $CuCl_2$, and $HgCl_2$ make it seem probable that the rate-determining step is the same in all three cases [Mitchell, *J. Chem. Soc.*, **121,** 1624 (1922) *et ante*]. The corresponding constants for the bromine and chlorine reactions are included for comparison.

Agent	k $(\text{moles/l})^{-1}\ \text{min}^{-1}$ at 25°C	k at 0.2°C
I_3^-	0.256	—
$CuCl_2$	.222	—
$HgCl_2$	.268	—
Br_2	.21	0.012
Cl_2	—	.029

The values of the constants for the moderately rapid follow-up reaction for the halogens have already been discussed in connection with the bromine reaction. No attempt has been made to isolate the two forms of hypophosphorous acid; further evidence of their reality is certainly a reasonable thing to search for.

The quantitative determination of hypophosphites may be accomplished by first oxidizing them to phosphates (for example, with H_2O_2 in warm alkaline solution) and then precipitating the phosphate by well-known methods. It is often more convenient, however, to make use of volumetric methods, and these have been repeatedly investigated, but most recently by Kolthoff [*Rec. trav. chim.*, **46,** 350 (1927)]. In one method, the hypophosphite solution is made neutral with $NaHCO_3$ and then treated with standard hypobromite solution; one-half hour is allowed for complete reaction. Potassium iodide and hydrochloric or sulfuric acid are then added. The liberated iodine is titrated with standard thiosulfate. A phosphate buffer would probably be superior to the bicarbonate. In another method a sulfuric acid solution of the hypophosphite is treated with excess standard permanganate, and after two hours' standing the excess permanganate is determined iodometrically or otherwise. In both methods the hypophosphite is oxidized to phosphate. Solutions containing only H_3PO_2 may be titrated with a strong base.

Phosphorous acid, H_3PO_3

The common form of phosphorous acid is the ortho-acid, H_3PO_3, but there does exist the meta-acid, HPO_2, which is formed when phosphine is burned in air. In aqueous solution HPO_2 goes over into the ortho-acid. Since the orthophosphorous acid is much the more common acid, it will be referred to simply as phosphorous acid. Phosphorous acid results when the anhydride P_4O_6 is shaken rapidly with ice water, but this does not provide the most convenient method for its preparation, since the P_4O_6 itself is not easily prepared.

Phosphorous acid is prepared by passing a stream of air through phosphorus trichloride, PCl_3, at 60° and then through ice-cold water. With 100 cc of water, the air stream should have such a velocity that about four hours are required for the formation of a nearly solid mass of H_3PO_3 crystals. This mixture is filtered by suction, and the residue is washed with small amounts of ice-cold water. The crystals are dried in a vacuum. The reaction of hydrolysis is

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl$$

The acid may also be prepared by adding PCl_3 to concentrated hydrochloric acid and then evaporating the resulting solution until the temperature reaches 180°. At this temperature all of the HCl is driven off and the solution contains mainly H_3PO_3 and some H_3PO_4.

Solid phosphorous acid melts at 71.7–73.6°, it will absorb moisture from the air and deliquesce, and it is very soluble in water. Per 100 g of solution, the accompanying weights S of H_3PO_3 are found in the saturated solutions.

t (°C)	S (g)
0	75.58
25.4	82.64
39.4	87.42

Much purer phosphorous acid may be prepared by treating lead phosphite with H_2S. Sodium phosphite is converted to the insoluble lead salt by mixing solutions of Na_2HPO_3 and lead acetate. After thoroughly washing the lead salt, $PbHPO_3$, a suspension of it in water is treated with H_2S, the resulting mixture is filtered, and the filtrate is heated to drive off the excess hydrogen sulfide. This solution will be practically free of phosphate, and it may be evaporated, if desired, to obtain crystals of H_3PO_3.

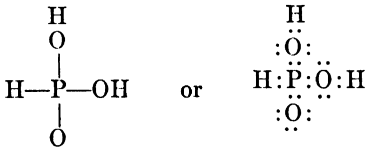
Both the pure acid and its concentrated solutions will decompose if heated strongly, the decomposition products being phosphine and orthophosphoric acid,

$$4H_3PO_3 = 3H_3PO_4 + PH_3$$

Atmospheric oxygen does not oxidize phosphorous acid solutions at ordinary temperatures at an appreciable rate; in the presence of iodine and light, oxygen will oxidize H_3PO_3 fairly rapidly, but this catalyzed reaction is slow in the dark.

Although phosphorous acid contains three atoms of hydrogen in the molecule, only two of them are capable of ionizing in aqueous solutions. The two ionization constants have been redetermined recently by Kolthoff [*Rec. trav. chim.*, **46**, 350 (1927)]. (See accompanying table.) Because phosphorous acid is only dibasic, it is supposed that one of the three hydrogens is bonded directly to the phosphorous atom:

Concentration (moles/l)	$K_1 \times 10^2$ at 18°	$K_2 \times 10^7$ at 18°
1 102	6.2	—
0 05	5.4	2 1
.01	3.9	2
.005	—	2
.002	2.8	—
.001	1.6	—



$$\begin{array}{c} H \\ O \\ | \\ H{-}P{-}OH \\ | \\ O \end{array} \quad \text{or} \quad \begin{array}{c} H \\ :\ddot{O}: \\ H:\ddot{P}:\ddot{O}:H \\ :\ddot{O}: \end{array}$$

Here, as in hypophosphorous acid, the coordination number of phosphorus is four rather than three.

As a consequence of its dibasic character and the fact that the second hydrogen ionizes less readily than the first, phosphorous acid forms two series of salts, of which $Na_2HPO_3{\cdot}5H_2O$ (m.p., 53°) and $NaH_2PO_3{\cdot}2\frac{1}{2}H_2O$ are representatives. The first of these is very soluble in water, 82.21 g per 100 g of solution at 25.2°, and the second to the extent of 56 g in 100 g of water at 0°. The lithium salt, $Li_2HPO_3{\cdot}H_2O$ is much less soluble, and its solubility, S, in g/100 g solution, decreases with increase in temperature, as shown in the tabulation. Lithium dihydrogen phosphite, LiH_2PO_3, is very soluble in water, as is also KH_2PO_3. The barium salt, $BaHPO_3{\cdot}\frac{1}{2}H_2O$, is sparingly soluble in water—only 0.6270 g in 100 g of solution at 30°—and thus differs from

t (°C)	S
0	9.07
25	7.47
50	6 09
98	4.24

the hypophosphite; the salt dissolves more freely in acids and ammonium chloride solutions, as is to be expected. Phosphorous acid is capable of forming complexes with a number of metals, for example, $KCr(HPO_3)_2 \cdot 12H_2O$. The phosphite phosphorus may act as a nucleus in such complexes as $Na_3[P(Mo_2O_7)_3] \cdot 10H_2O$.

When sodium phosphite, $NaH_2PO_3 \cdot 2\frac{1}{2}H_2O$, is heated in a vacuum at 160° until water is no longer lost, sodium pyrophosphite, $Na_2H_2P_2O_5$, is formed. This salt is soluble in water, and the solutions are quite stable at ordinary temperatures, but on boiling, hydrolysis to the orthophosphite takes place. In acid solution, the rate of hydrolysis is more rapid but is still measurable.

Phosphorous acid in aqueous solution is a very strong reducing agent, although frequently it reacts but slowly with the oxidizing agents. For example, it reduces Ag^+ to metallic silver, and it reacts with hot concentrated sulfuric acid to form H_3PO_4 and SO_2. At room temperatures it reacts at slow but measurable rates with the halogens, dichromate, and mercuric chloride, and only very slowly if at all with peroxysulfate unless iodine or silver ion is present. At 60–70° sulfurous acid is reduced to sulfur and some hyposulfurous acid by phosphorous acid. The oxidation potential of the couple, H_3PO_3, H_3PO_4, in acid solution is estimated by Latimer [*Oxidation Potentials*] to be 0.20 volts; in alkaline solution the potential $HPO_3^=$, $PO_4^≡$ is given as 1.05 volts.

The rate of oxidation of phosphorous to phosphoric acid by the halogens has been investigated carefully by Mitchell [*J. Chem. Soc.*, **123,** 2241 (1923)], Berthoud and Berger [*J. Chim. Phys.*, **25,** 568 (1928)], and Griffith and McKeown [*Trans. Faraday Soc.*, **29,** 611 (1933)]. The mechanisms proposed for the three reactions differ in that tautomeric forms of H_3PO_3 are assumed by Mitchell (but not by Berthoud and Berger) in the iodine reaction, and a difference in reactivity of $H_2PO_3^-$ and $HPO_3^=$ with the halogen is assumed in the bromine and chlorine reactions. The latter mechanism seems somewhat more acceptable, and it appears likely that the iodine reaction can be explained by means of it also.

The equation for the main reaction is, in the case of bromine,

$$H_3PO_3 + Br_2 + H_2O = H_3PO_4 + 2H^+ + 2Br^-$$

and the experimentally established rate equation has the form

$$\frac{d(H_3PO_4)}{dt} = k_1(H_2PO_3^-)(Br_2) + k_2(HPO_3^=)(Br_2)$$

Molecular bromine, Br_2, and not Br_3^- or HBrO, is the reactive bromine compound. The constants have the following values:

$$k_1 = 10.1 \left(\frac{\text{mole}}{1}\right)^{-1} \text{min}^{-1} \text{ at } 10°\text{, and } 25.3 \text{ at } 20°$$

$$k_2 = 4.8 \times 10^7 \left(\frac{\text{mole}}{\text{l}}\right)^{-1} \text{min}^{-1} \text{ at } 10°, \text{ and } 916 \times 10^7 \text{ at } 20°$$

The investigation of the chlorine reaction presents some difficulties, and the values of k_1 and k_2 are not given. Empirically the rate may be expressed by

$$\frac{d(H_3PO_4)}{dt} = k(\Sigma Cl_2)(\Sigma H_3PO_3)$$

and k has the accompanying representative values at 10°. Concentrations are expressed in moles per liter and the time in minutes. The reader may assure himself that the rate equation and the constants k for the chlorine reaction are not altogether inconsistent with the mechanism assumed for the bromine reaction. It is of interest that neither HClO nor HBrO is a reactant in the rate-determining steps. These intermediates are formed in the rate-determining steps of many reactions in which an oxyacid oxidizes a halide, X^-; they are the active reactants in the oxidation by halogens in several reactions, but they are not invariably the intermediates in all halogen reactions, as the hypophosphorous and phosphorous acid oxidations show.

(HCl)	(NaCl)	k
0.1265	0.8855	4.73
.2025	.813	2.63
.253	.762	2.075
.354	.661	1.402
.506	.508	0.9145
1.012	0.0	.3924

It cannot be said that the mechanism of the iodine reaction has been firmly established. Mitchell postulates two tautomeric forms of H_3PO_3 to explain his results, but it is not certain that this is necessary. Empirically the rate equation is

$$\frac{d(H_3PO_4)}{\cdot dt} = k_1(I_2)(\Sigma H_3PO_3) + \frac{k_2(\Sigma H_3PO_3)}{1 + k_3/(I_3^-)}$$

k_1, k_2, and k_3 being somewhat dependent on (H^+) and other factors as well. The following values at 25° will give an idea of the order of magnitude of the rate. Concentrations are expressed in moles per liter of solution and the time is in hours.

(H^+)	k_1	k_2	k_3
0.0502	2.98	0.00189	0.0025
.1255	2.00	.00465	.0048
.1063	2.01	.00294	.0025
.0829	1.93	.00385	.0040
.1533	1.65	.00682	.0060

At high acid concentrations, the reaction becomes so slow that weeks may be required for its completion.

When iodine is used for analytical purposes, the solutions should be nearly neutral or slightly alkaline. The most satisfactory method of volumetric analyses for the phosphites makes use of iodine as an oxidizer and of a phosphate buffer which is so adjusted that the solution is faintly acid. A phosphate buffer is superior to a sodium bicarbonate buffer because the latter cannot be safely acidified for the purposes of the thiosulfate titration of the excess iodine [Van Name and Huff, *Am. J. Sci.*, 91 (1918)].

The iodine reaction was studied by Berthoud and Berger (*loc. cit.*) in both acid and neutral solutions, and it is their conclusion that the mechanism is not the same in the two cases. Their experiments were carried out with such an excess of H_3PO_3 or Na_2HPO_3 over the iodine that the phosphite concentration did not change appreciably during a run. In acid solution the rate equation is

$$H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2H^+ + 2I^-$$

$$-\frac{d(\Sigma I_2)}{dt} = k_a(\Sigma I_2)(H_3PO_3)$$

k_a increases slightly with acid concentration but is not affected by changes in (I^-), which suggests that the active reactants are H_3PO_3, undissociated, and both I_2 and I_3^-. The values of k_a at 35° for mixtures of varying (HCl), but all having initially $(I^-) = 0.1$ n, $(H_3PO_3) = 0.2$ m, $\Sigma I_2 \approx 0.005$ m, are shown in the table (concentrations in moles/l and time in minutes). At 25° and 45°, k_a has the values 0.0094 and 0.097, respectively. The small variation of k_a with (H^+) is effectively removed when the ionization of the H_3PO_3 is taken in account. In acid solution an approximate mechanism is then represented by the equation

(HCl)	$k_a \times 10^2$
0 1	3 36
.2	4.0
.5	4 6
.1 (H_3PO_3 = 0.4)	3.86

$$H_3PO_3 + I_2 \text{ (and } I_3^-) + H_2O = H_3PO_4 + 2H^+ + 2I^-$$

In nearly neutral solutions, the rate of oxidation of phosphites is much more rapid than in acid solution; and since in acid solution the rate depends but little on the acid concentration, the much greater rate in nearly neutral solutions suggests that the mechanism is different in the two cases. The following rate constants k_n are defined by the equation

$$-\frac{d(\Sigma I_2)}{dt} = k_n(\Sigma I_2)(\Sigma H_3PO_3)$$

In the neutral solutions the phosphite is present principally as $HPO_3^{=}$ and $H_2PO_3^-$. The initial concentration of iodine was $\Sigma I_2 \approx .01$ m. The dependence on (I^-) is not one of simple inverse proportionality, but rather one in which $k_n = k_1 + k_2/(I^-)$, and this indicates that I_2 and I_3^- react at different rates with the hypophosphites; I_2 reacts the more rapidly.

Na_2HPO_3 = 0.0833 m, HAc = 1 n, NaAc = 0.5 n, t = 25°

(KI)	k_n
0.166	0.48
.3058	.30
.666	.20

The effect of changes in (H^+) in the buffered solutions is shown by the results in the second table. It is evident that k_n increases more rapidly than in direct proportion to the concentration of hydrogen ion. Finally, the effect of hypophosphite concentration is to be seen in another series of experiments. In this case the constants have been corrected for the effect of Na_2HPO_3 on the concentration of H^+. The lack of complete constancy in k_n here may indicate that the $H_2PO_3^-$ and $HPO_3^{=}$ ions react at different rates with I_2 or I_3^-. No account has been taken, however, of the effect of total salt concentration, a fact which may account for such variations in k_n as are observed. A complete and accurate analysis of all of the rate data for the iodine reaction has not been made, but, according to Berthoud and Berger, a fairly satisfactory mechanism consists of the two following reactions:

Na_2HPO_3 = 0.0833 m, KI = 0.1 n, NaAc = 0.5 n, t = 0°

(HAc)	k_n
0.25	0.184
.5	.078
1.0	.030

$$HPO_3^{=} + I_2 + OH^- = H_2PO_4^- + 2I^-$$
$$H_2PO_3^- + I_2 + OH^- = H_3PO_4 + 2I^-$$

and similar equations with I_3^- in place of I_2. The fact that k_n increases with total salt concentration could be regarded as evidence for one or more reactions between ions of like sign. The first of these reactions would be more rapid than the second. In acid solution the concentration of OH^- would be too low for these reactions to be important, and in neutral or alkaline solution the concentration of undissociated H_3PO_3 is so small that the direct reaction with it is negligible. A very thorough investigation of the iodine reaction should clear up many points that are obscure.

KI = 0.1 n, HAc = 0.5 n, NaAc = 0.5 n, t = 0°

(Na_2HPO_3) (mole/l)	k_n
0.04166	0.056
.0833	.059
.166	.074

Phosphorous acid reacts slowly with mercuric chloride to form phosphoric acid and mercurous chloride according to the equation

$$H_3PO_3 + 2HgCl_2 + H_2O = H_3PO_4 + 2H^+ + 2Cl^- + 2HgCl$$

The rate increases with increase in acid concentration, and the reaction is first-order with respect to phosphorous acid but is a more complicated function of the concentration of mercuric chloride [Linhart, *Am. J. Sci.*, **35**, 353 (1913)]. In hydrochloric acid solution, it is known that mercuric chloride exists in the form of complexes, principally as $H_2Hg_2Cl_6$ together with other less well-established compounds. If it is assumed that the active reactant is $HHgCl_3$, and that it is in equilibrium with $H_2Hg_2Cl_6$ according to the equation

$$H_2Hg_2Cl_6 = 2HHgCl_3$$

and further that the slow reaction is

$$H_3PO_3 + HHgCl_3 = H_2PO_3 + 2H^- + 2Cl^- + HgCl$$

then, if the rapid follow-up reaction is

$$2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4$$

the rate equation takes the form

$$\frac{d[\mathrm{HgCl}]}{dt} = k'(\mathrm{H_3PO_3})(\mathrm{HHgCl_3})$$

It is assumed further that both $H_2Hg_2Cl_6$ and $HHgCl_3$ ionize freely into H^+, $Hg_2Cl_6^=$, and $HgCl_3^-$, so that the concentration of $HHgCl_3$ is small, and

$$(\mathrm{HHgCl_3}) = K_1(\mathrm{H^+})(\mathrm{HgCl_3^-})$$

In addition to this relation,

$$(\mathrm{HgCl_3^-}) = K_2(\mathrm{Hg_2Cl_6^=})^{1/2}$$

Using these relations in the rate equation, there results

$$\begin{aligned}\frac{d[\mathrm{HgCl}]}{dt} &= k'K_1K_2(\mathrm{H_3PO_3})(\mathrm{H^+})(\mathrm{Hg_2Cl_6^=})^{1/2}\\ &= k(\mathrm{H_3PO_3})(\mathrm{H^+})(\mathrm{Hg_2Cl_6^=})^{1/2}\end{aligned}$$

The values of *k* obtained by Linhart are shown in the following table together with the initial concentrations, in moles per liter of solution, of the reactants. The time is expressed in minutes.

$HgCl_2$	H_3PO_3	HCl	t (°C)	$k \times 10^2$
0.132	0.0575	0.264	60	18.9
"	"	.132	"	20.7
"	"	.100	"	22.0
"	0.0585	2.000	25	0.40
"	"	1.000	"	.256
"	"	0.500	"	.278
"	"	.264	"	.278 to .315
"	"	.132		.32–.34

When it is considered that the initial concentrations of the electrolytes are rather large and vary over a large range, and hence the salt effects may be appreciable, the values of k are satisfactorily constant. The one disquieting thing about the mechanism involves the rapid follow-up decomposition of metahypophosphoric acid.

$$2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4$$

The common form of this acid is $H_4P_2O_6$, and its rate of decomposition at room temperature is quite slow in dilute acid solutions. Nothing is known about the metahypophosphoric acid, and it must be assumed that two H_2PO_3 will combine with water to form H_3PO_3 and H_3PO_4 rather than form the less reactive dimer $H_4P_2O_6$. This does seem curious but, of course, is not impossible, so far as we know. It must be obvious by now that the mechanisms of reactions frequently involve steps which resist detailed study, and this is not a very satisfactory state in which to leave them. We are not able, at this time, to do any better.

Hypophosphoric acid, $H_4P_2O_6$

This acid is not formed when phosphorus tetroxide is dissolved in water, although this oxide would appear to be its anhydride. The reason for this result may be that the heat developed at the surface of the P_2O_4, upon reaction with water, brings about the decomposition of any $H_4P_2O_6$ that may be formed at first. The reaction of P_2O_4 with water is $P_2O_4 + 3H_2O = H_3PO_3 + H_3PO_4$, and acid solutions of $H_4P_2O_6$ hydrolyze slowly to give the same products.

Hypophosphoric acid can be prepared by partially submerging sticks of white phosphorus in water or sodium acetate solution and allowing air to have limited access to the mixture. Ordinarily, holes are forced lengthwise through the phosphorus sticks and knotted strings threaded through the holes. The sticks are suspended by the strings in the sodium acetate solution so that only about one centimeter of the length is above the liquid and exposed to the air. When the exposed phosphorus is oxidized, a further length is exposed by raising the string. A many-holed porcelain plate provided with corks may be used to hold the upper ends of the strings, and if the plate rests on the beaker of solution and a few of the holes are left unstoppered, the sticks may be raised readily and proper access of air will be provided [Bansa, *Z. anorg. Chem.*, **6**, 132 (1894); *Ber.*, **39**, 2837 (1906)]. As a result of the oxidation of the phosphorus under these conditions, there is formed phosphorous, hypophosphoric, and phosphoric acids, which, with the sodium acetate solution, form the acid salts. The salt $Na_2H_2P_2O_6{\cdot}6H_2O$ is much less soluble in water (2 g/100 g H_2O) than are $NaH_2PO_3{\cdot}2\frac{1}{2}H_2O$ and $NaH_2PO_4{\cdot}H_2O$, and it forms a crystalline precipitate on the bottom of the beaker. This precipitate is washed and recrystallized to purify it. By treating a solution of the sodium salt with lead acetate, the slightly soluble, white lead hypophosphate is formed; and after careful washing, this can be suspended in water and treated with hydrogen sulfide to obtain a solution of hypophosphoric acid alone. On evaporating this solution in a vacuum desiccator containing calcium chloride, rhombic crystals of the hydrated free acid $H_4P_2O_6{\cdot}2H_2O$ are obtained.

Hypophosphoric acid may also be prepared by causing nitric acid solutions of silver or copper nitrate to react with white phosphorus.

A method developed by Rosenheim and Pinsker [*Ber.*, **43,** 2003 (1910)] consists in the anodic oxidation of copper phosphide (14% P) in a 2% solution of sulfuric acid with a potential of 3–10 volts. Copper metal is used as a cathode. The yield is about 60%, the remainder of the phosphorus being converted to orthophosphoric acid. Very little if any phosphorous or hypophosphorous acid is formed if the potential applied is 3 volts or above. Copper ions are formed in the oxidation but are readily removed by electrolysis with plain platinum electrodes.

Another and more convenient method for the preparation of hypophosphates is that of Probst [*Z. anorg. Chem.*, **179,** 155 (1929)], in which red phosphorus is slowly added to a well-stirred and cooled (5°) solution which is 0.2 m in NaOH and 1.5 m in NaClO. The reaction is

$$4NaClO + 2P\ (red) + 2H_2O = 4NaCl + H_4P_2O_6$$

and a 25% yield of pure $Na_2H_2P_2O_6{\cdot}6H_2O$ is obtainable.

Pure, hydrated hypophosphoric acid is a colorless, deliquescent solid which decomposes on heating into H_3PO_3 and H_3PO_4 and which is very soluble in water. The aqueous solutions are not affected by atmospheric oxygen and when cold do not decompose at a measurable rate; when heated, decomposition into H_3PO_3 and H_3PO_4 takes place.

The ionization constants of the acid have been determined by Treadwell and Schwarzenbach [*Helv. Chim. Acta,* **11,** 405 (1928)] by an electromotive force method. For purposes of comparison, approximate ionization constants of ortho- and pyrophosphoric acid are also included in the following table.

TABLE 51
IONIZATION CONSTANTS OF HYPO-, ORTHO-, AND PYROPHOSPHORIC ACIDS

	K_1	K_2	K_3	K_4
$H_4P_2O_6$	$10^{-2.2}$	$10^{-2.81}$	$10^{-7.27}$	$10^{-10.03}$
$H_4P_2O_7$	$10^{-0.85}$	$10^{-1.96}$	$10^{-6.54}$	$10^{-8.44}$
H_3PO_4	$10^{-1.96}$	$10^{-7.24}$	$10^{-12.0}$	—

One concludes from these results that hypophosphoric acid is not very strong and that in its successive ionizations it resembles pyrophosphoric acid. Of interest is the fact that K_1 and K_2 for $H_4P_2O_6$ are not greatly different; this suggests but does not prove that the structure of the acid is symmetrical with respect to two OH groups. The freezing points of hypophosphoric acid are not in accord with the ionization constants of Treadwell and Schwarzenbach, as the following results of Rosenheim and Pinsker show [*Ber.*, **43**, 2003 (1910)], where C is the molar concentration, ΔT is the observed freezing-point lowering, and α is the degree of ionization calculated on the assumption that the molecular species present result mainly from the reaction

$$H_4P_2O_6 = 2H^+ + H_2P_2O_6^=$$

In arriving at values for α, the state of the solutions has doubtless been oversimplified, but certainly the freezing-point lowerings show much greater ionization than the values of K_1 and K_2 in Table 51 permit. Moreover, the molar conductances at 25.6° of $H_4P_2O_6$ do not differ greatly from those of the presumably stronger acid $H_4P_2O_7$, and this fact indicates that the two acids are of approximately equal strength. It can scarcely be said that the data are in accord; no definite statement about the ionization constants K_1 and K_2 can be safely made yet.

C	ΔT (°C)	α
0.612	1.947	0.36
.228	0.764	.40
.131	.471	.46
.0158	.065	.60
.0079	.035	.69

C (mole/l)	$\Lambda_{H_4P_2O_6}$	$\Lambda_{H_4P_2O_7}$
0.050	329.4	353.8
.0125	417.6	438.6
.00125	589.7	602.0

Salts of the type $Li_4P_2O_6 \cdot 7H_2O$, $Na_4P_2O_6 \cdot 10H_2O$, $Na_2NiP_2O_6 \cdot 12H_2O$, $Na_3HP_2O_6 \cdot 9H_2O$, and $Na_2H_2P_2O_6 \cdot 6H_2O$ are well known, and their existence shows that all four hydrogens are capable of ionizing; hypophosphoric acid is a tetrabasic acid.

The formula for hypophosphoric acid was not established with any certainty until recently. It has been argued on the basis of the above conductance and freezing-point data that the formula was simply H_2PO_3; the same data, together with the results of rate measurements, have been cited as evidence for the doubled formula $H_4P_2O_6$. If the formula were H_2PO_3, the molecule would contain an odd number of extranuclear electrons and hence would be paramagnetic. Bell and Sugden [*J. Chem. Soc.*, 48 (1933)] found, however, that the hypophosphates $Na_2H_2P_2O_6$, $Na_2H_2P_2O_6 \cdot 6H_2O$, $Ag_4P_2O_6$, and $(CN_3H_5)_4H_4P_2O_6 \cdot 2H_2O$ are all diamagnetic, and therefore the doubled formula, $H_4P_2O_6$, is the one to be accepted.

It has already been remarked that sodium dihydrogen hypophosphate is much less soluble in water than are the corresponding phosphite and phosphate. This slight solubility extends to the normal lithium salt and other sodium salts, as the following values show. The potassium salts are more soluble than the corresponding sodium salts.

Temp. (°C)	$Li_4P_2O_6 \cdot 7H_2O$ (g/100 g soln.)	$Na_4P_2O_6 \cdot 10H_2O$ (g/100 g H_2O)	$Na_3HP_2O_6 \cdot 9H_2O$ (g/100 g H_2O)	$Na_2H_2P_2O_6 \cdot 6H_2O$ (g/100 g H_2O)
0	0.1018	—	—	—
25	.0575	1.49 (25.2°)	4.67	2.00
30	—	1.72	—	—
35	—	—	7.16	3.08
40	.0480	2.27 (40 2°)	—	—
50	—	3.18	14 96	5.95

The trihydrogen hypophosphates appear not to exist. The guanidine salt, $[NHC(NH_2)_2]_4H_4P_2O_6 \cdot 2H_2O$, is soluble to the extent of only 1.038 g/100 cc soln. at 28.5°. Of interest is the only known silver salt $Ag_4P_2O_6$; it is practically insoluble in water and in hypophosphoric acid solutions, and is only sparingly soluble in dilute nitric acid. It will dissolve in ammonia solution, however. No acid salts of silver are known; they do not appear capable of existence.

Solutions of the salts are much more stable toward decomposition than are those of the acid. The rate of decomposition of the acid alone is too slow to be measured at room temperature, but in the presence of added acid the rate is increased. At 60° the rate is measurable when the concentration of added acid is as low as 0.25 n. It was found by Van Name and Huff [*Am. J. Sci.*, **45**, 91, 103 (1918)] that the decomposition reaction is quite accurately of the first order if added acid is present in excess, and that the rate constants increase with increase in concentration of acid. The following values of the rate constants are averages of those given by Van Name and Huff; the maximum deviations of individual values from the average are about $\pm 2\%$ or less. Their reaction mixtures were made by mixing solutions of hydrochloric acid with portions of a 0.05 n $Na_2H_2P_2O_6$ stock solution in the proportions desired. The normal concentrations of the reactants have been computed from their data. The solutions were analyzed by adding to them excess standard iodine after being made neutral and adding NaH_2PO_4 as a buffer; the iodine oxidizes H_3PO_3 but not $H_4P_2O_6$ to phosphate. The excess iodine was determined with thiosulfate. The main reaction is

$$H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4$$

and

$$\frac{d(H_3PO_3)}{dt} = k(H_4P_2O_6)$$

TABLE 52
THE RATE OF DECOMPOSITION OF $H_4P_2O_6$ IN HYDROCHLORIC ACID SOLUTION

Temperature	Conc. $H_4P_2O_6$ (moles/l)	Conc. HCl (moles/l)	$k \times 10^4$ (min^{-1})	$k/(\text{HCl})^2$ $\times 10^4$
25°	0.025	4.66	10.3	0.48
	.025	5.0	12.5	.50
	.013	2.5	1.86	.30
60°	0.013	2.5	63.1	10.1
	.013	0.265	0.76	10.9

The calculated values of $k/(\text{HCl})^2$ are shown in the last column, and their approximate constancy indicates that the reactant is $H_4P_2O_6$ and that much of the hypophosphoric acid is ionized into $2H^+ + H_2P_2O_6^=$. As a consequence of this assumed ionization, one sets $(H_4P_2O_6) = K(H^+)^2 (H_2P_2O_6^=)$, and the rate equation given above becomes

$$\frac{d(H_3PO_3)}{dt} = kK(H^+)^2(H_2P_2O_6^=) = k'(H^+)^2(H_2P_2O_6^=)$$

The small variation of k' with the concentration of acid may be due to neutral salt effects. In view of the previous discussion, it cannot be decided definitely now whether the assumption of extensive ionization of $H_4P_2O_6$ is in accord with the facts; accordingly, the proposed mechanism must be regarded as tentative. It is desirable that the ionization of hypophosphoric acid be studied further. It must be remembered, too, that the mechanism of the acid hydrolysis of many substances is obscure, for example, $H_2S_2O_6$, and it may be that the ionization hypothesis is overworked in attempting to arrive at explanations for the observed rates.

As a reducing agent, hypophosphoric acid is not very reactive. Thus, it is not oxidized by the halogens or even by boiling dichromate. Permanganate oxidizes hypophosphates slowly at room temperature and more rapidly when heated. For the purposes of analyses, the permanganate method is moderately satisfactory but is held in less esteem than the decomposition method. In the latter, the hypophosphate is heated nearly to dryness with hydrochloric acid, and the phosphorous acid formed is oxidized with excess standard iodine in a solution buffered with phosphate. Silver hypophosphate, $Ag_4P_2O_6$, is only slightly soluble in water, and may be made the basis for a gravimetric method of analysis [see Probst, *Z. anorg. Chem.*, **179**, 155 (1929)].

Phosphoric acids

The preparation of these acids has been described in connection with the recovery of phosphorus from phosphates. It is only necessary to add that when the pentoxide, P_4O_{10}, the pentahalides, or the pentavalent oxyhalides are treated with water, rapid hydrolysis sets in with the formation of phosphoric acids. The oxidation of the lower acids to phosphoric acid has already been discussed. Inasmuch as the reduction of the phosphoric acids is accomplished only with very powerful reducing agents, we shall concern ourselves here principally with the properties and structure of the acids themselves rather than with their oxidation-reduction chemistry.

There are a number of phosphoric acids which differ for the most part in their degree of hydration and polymerization. The following list contains those which, for one reason or another, are believed to exist; in some cases only the salts are stable to eventual hydrolysis. There are doubtless other phosphoric acids whose formulas have not yet been firmly established.

$(HPO_3)_n$	n-metaphosphoric acid
$(HPO_3)_6$	Hexametaphosphoric acid
$(HPO_3)_4$	Tetra meta phosphoric acid
$(HPO_3)_3$	Trimetaphosphoric acid
$(HPO_3)_2$	Dimetaphosphoric acid
HPO_3?	Metaphosphoric acid
$H_4P_2O_7$	Pyrophosphoric acid
$H_5P_3O_{10}$	Triphosphoric acid
H_3PO_4	Orthophosphoric acid

Metaphosphates

When phosphorus pentoxide is treated with a small amount of water, or when phosphoric acid is strongly heated, the polymetaphosphoric acids, $(HPO_3)_n$, are formed. Sodium salts may be made by neutralizing the acids, or directly by heating NaH_2PO_4, $Na_2H_2P_2O_7$, or $NaHNH_4PO_4$ under various conditions. The polymetaphosphates form a very complex system, and the question of the molecular species that exist has been an outstanding and difficult puzzle in inorganic chemistry. The literature is extensive and contradictory, and much more experimental work must be done before the present confusion can be cleared up.

One of the difficulties in the study of the subject is the lack of uniformity in naming compounds. A single salt prepared in a definite way may be referred to as mono-, tri-, or hexametaphosphate, according to the theories of the author. To clarify the following discussion as much as possible, a table is given of the compounds which seem to have a reasonable claim to be considered definite species. The names given conform as far as possible with the customary usage in the literature and will be used consistently throughout. Each compound is characterized by its method of preparation and a limited number of reactions.

TABLE 53
THE SODIUM METAPHOSPHATES

Name	Probable Polymer	Methods of Preparation	Properties
Pascal's salt	?	$(C_2H_5PO_3)_n + C_2H_5ONa$ in ether solution.	White, deliquescent solid; soluble in water; ppts. with Ag^+, Pb^{++}, Ca^{++}; coagulates albumin.
Sodium dimetaphosphate	di	1. Heat H_3PO_4 a short time at about 300°, neutralize cold solution. 2. Heat NH_4NO_3 (1 pt.), NaH_2PO_4 (5 pts.), and NH_4Cl (1 pt.) at 250°.	Soluble in water but hydrolyzes rapidly to pyrophosphate; ppts. with Pb^{++} but does not coagulate albumin.
Maddrell's salt	?	Heat NaH_2PO_4 at 300–400° for several hours.	Crystalline, insoluble solid; two crystalline modifications.
Knorre's salt or sodium trimetaphosphate	tri	1. Heat NH_4NO_3 (1 pt.) and NaH_2PO_4 (2 pts.) at 300°. 2. Heat NaH_2PO_4 at 500–600° for several hours. 3. Heat fused Graham's salt at 300–400° for a few hours.	White, soluble crystalline substance, m.p. 625°; no ppt. with Ag^+ or Pb^{++} in low concentration; no ppt. with Ca^{++}, coagulates albumin.
Sodium tetrametaphosphate	tetra	Heat CuO and H_3PO_4 up to 400°. Treat copper salt with H_2S and neutralize.	White soluble substance; ppts. Pb^{++} and Ca^{++} but not Ag^+. Coagulates albumin.
Graham's salt or sodium hexametaphosphate	hexa	NaH_2PO_4, $Na_2H_2P_2O_7$, or $NaNH_4HPO_4$ fused and quenched.	Easily soluble glass; ppts. with Ag^+, Pb^{++}, but forms stable complex ion with Ca^{++}.
Kurrol's salt	>hexa	Obtained sometimes on heating NaH_2PO_4 below fusion for long periods of time. Potassium salt made readily by heating KH_2PO_4 to above 300°.	Insoluble in water but dissolves in solutions of pyro- and hexametaphosphate to give highly viscous solutions. Melts at 809° to give liquid distinct from melted Graham's salt. The cooled melt is an insoluble glass.

If glacial phosphoric acid is warmed for a short time at about 300° until a very thin crust appears on the surface, the resulting mixture consists of an insoluble solid polymer and a soluble liquid. If the heating is stopped at the first appearance of a solid, the product dissolved in ice water, and the calculated amount of base added, a clear, almost neutral solution results [Pascal and Rèchid, *Compt. rend.*, **196**, 828 (1933)]. An excess of alcohol will precipitate an oil which soon crystallizes. The resulting crystals are very soluble in water but hydrolyze quickly to pyrophosphate at room temperature. Tests made immediately after the solution in ice water show that the salt is not pyrophosphate, as determined by the solubility of the zinc salt in alkaline solution and by the absence of a precipitate with Co $(NH_3)_6Cl_3$ in neutral solution. (Pyrophosphates give a reddish-yellow precipitate with the cobalt complex; the test is a most useful one, as none of the metaphosphates give precipitates.) The salt does not coagulate albumin, as do the higher metaphosphates. The freezing-point lowering indicated a molecular weight of 130 for a $\frac{1}{10}$ normal solution and 76 for a $\frac{1}{32}$ normal solution. These facts are moderately consistent with the assumption that the salt is a dimetaphosphate; if it were completely ionized, its molecular weight would be 68. Analyses gave the empirical formula $(NaPO_3)_2{\cdot}3H_2O$. When the hydrated salt is heated, first some acid pyrophosphate and then the insoluble Maddrell salt is formed. Further heating gives the same products as the NaH_2PO_4 system discussed later.

Travers and Chu [*Compt. rend.*, **198**, 2100 (1934)] repeated the above work, and they state that the product obtained is always contaminated with some pyrophosphate. They were able, however, to prepare the dimeric salt by mixing 5 parts of Na_2HPO_4, 1 part of NH_4NO_3, and 1 part of NH_4Cl and heating in a vacuum at 250° for eight hours. The product was slowly cooled and dissolved in water with the aid of a few drops of acid or base. The resulting solution was made neutral to methyl orange, and the pure salt was separated from the more soluble pyrophosphates by several crystallizations. Freezing-point determinations gave a molecular weight of 68 with 30 g of salt per liter (0.23 n) and 69.6 with 40 g per liter (0.31 n). By treating the crystallized lead salt with hydrogen sulfide, the free acid was obtained; its aqueous solutions hydrolyze slowly at 0° and more rapidly at higher temperatures. The authors state that the hydrolytic reaction

$$H_2O + H_2P_2O_6 = H_4P_2O_7$$

was shown to be first-order at temperatures below 66°, where the hydrolysis of the pyrophosphoric acid could be neglected.

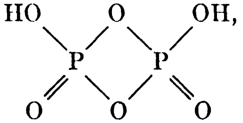
Liquid dimetaphosphoric acid is not stable, especially at high temperatures [Rèchid, *Compt. rend.*, **196**, 860 (1934)], and if heating is continued at temperatures less than 400°, crystals of some different polymer begin to form. The phenomenon is evident in about 20 hours at 218° and in a half-hour at 355°. The new substance is crystalline according to X-ray evidence, it is insoluble in water and warm dilute nitric acid, and it is soluble with hydrolysis in boiling sodium hydroxide. It may be warmed to 800° without melting or giving off perceptible vapors. The exact nature of this polymer is obscure.

If, on the other hand, the dimetaphosphoric acid, or the glacial orthophosphoric acid from which it is made, is heated above 400°, a transparent, soluble polymer transformable reversibly to the insoluble polymer is formed. The molecular weight of the soluble polymeric acid, as determined from its salts, increases and the solubilities of the salts decrease progressively with higher temperatures and increased duration of heating. For example, the molecular weight of the sodium salt of an acid heated four hours at 600° was 358. If the soluble polymer is heated to red heat for several hours, the so-called *crackly acid* is formed; this acid when treated with water makes a crackling sound, and the water becomes turbid with the small white particles shot off. The turbidity is slow to clear up and the solid is slow to disperse; consequently, complete solution results only after a long time. All of the soluble polymeric acids coagulate albumin, and all are uncrystallizable, as are also their salts. The soluble polymer formed by heating above 400° distinguishes itself from the insoluble polymer formed by long heating below 400° by its greater volatility. However, even the high molecular-weight polymers are decomposed on vaporization, and the vapor density at white heat corresponds to the dimeric compound $(HPO_3)_2$ [Tilden and Barnett, *J. Chem. Soc.*, **69**, 154 (1896)]. The quickly condensed vapor is identical in properties with dimetaphosphoric acid.

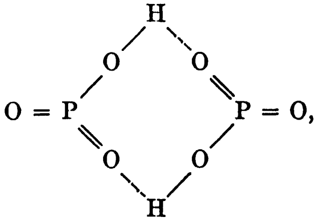
PASCAL'S SALT. PREPARED AT ROOM TEMPERATURES

g/100 g H_2O	$-\Delta T$	Molecular Weight
0.360	0.126°	52.8
.618	.207	55.2
.953	.290	60.8
Same $NaPO_3$ Heated to 250°		
0.360	0.128°	52.0
Same $NaPO_3$ Melted at 900°		
0.360	0.139°	48.0

It seems likely that the structure of the dimer is



and the strong P—O—P bonds are responsible for the stability of the molecule. A structure containing hydrogen bonds,



would hardly be stable enough to correspond to the known properties of $(HPO_3)_2$.

In view of the great stability of the dimer in the vapor phase and of its tendency in the liquid phase to polymerize, the existence of a monomer would hardly be expected under any conditions. However, a compound which was believed to be a monometaphosphate was prepared by Pascal [*Bull. soc. chim.*, **33,** 1611 (1923)]. The first step in its preparation consists in boiling a mixture of ether and P_2O_5 to obtain the compound $(C_2H_5PO_3)_n$. This substance on treatment with C_2H_5ONa in ether reacts to form $(C_2H_5)_2O$ and a sodium metaphosphate. The evidence that Pascal's salt is a monometaphosphate is the freezing-point lowerings above (p. 213) found for the aqueous solutions. Since the formula weight of $NaPO_3$ is 102, the completely ionized salt would show an effective molecular weight of $\frac{102}{2} = 51$, and the observed values are in accord with this number. However, Nylèn [*Z. anorg. Chem.*, **229,** 30 (1936)] made two preparations of the salt according to Pascal's directions and obtained the freezing-point lowerings in the second table. The calculated, effective molecular weights for the different polymers assuming complete ionization are given for reference:

PASCAL'S SALT. PREPARED AT ROOM TEMPERATURE

	g/100 g H_2O	$-\Delta T$	Molecular Weight
I	0.186	0.040°	86.5
	.348	077	84.1
	.524	.114	90.0
II	.147	.036	88.2
	.298	.070	92.5
	.416	.093	94.5

Polymer	Molecular Weight
mono	51.0
di	68.0
tri	76.5
tetra	81.6
penta	85.0
hexa	87.4

It is apparent that the results of Nylèn disagree completely with those of Pascal. It is difficult to interpret the data, but they indicate that the salt is not a monometaphosphate. Nylèn confirmed the chemical properties given by Pascal. Pascal's salt is a white, hydroscopic, amorphous powder easily soluble in water to give a neutral solution. It yields white precipitates with silver, lead, and barium but not with $Co(NH_3)_6Cl_3$, and it coagulates albumin. The reported chemical and physical properties of this substance are not those of any other recognized polymetaphosphate, although they seem most like those of hexametaphosphate. The exact nature of the salt is a matter for further study.

Before the nature of the polymetaphosphates was better understood, it was believed that a monometaphosphate could be prepared by fusing microcosmic salt ($NaNH_4HPO_4$), NaH_2PO_4, or $Na_2H_2P_2O_7$. For example, Beans and Kiehl [*J. Am. Chem. Soc.*, **49**, 1878 (1927)] heated one of these salts for an hour at 200° to dehydrate it, and then they heated it slowly to about 600° until fusion took place. After ten or fifteen minutes at about 600°, the substance was cooled to 450°, when, in about two hours, monoclinic crystals of a metaphosphate formed. The resulting salt is soluble in water and, when purified by recrystallization, gives solutions which are slightly acid, $(H^+) = 2 \times 10^{-6}$ [Kiehl and Hill, *J. Am. Chem. Soc.*, **54**, 1332 (1932)]. The accompanying freezing-point lowerings were obtained by Beans and Kiehl with aqueous solutions of their salt.

$g/100\ g\ H_2O$	$-\Delta T$	Molecular Weight
5.0472	0.916°	102.5
2 8159	.546	96.9
1 3435	.351	71 2

The probable nature of this salt may be determined from a consideration of the equilibrium studies on the sodium metaphosphates. Investigations have been made by three groups, who, however, disagree on several points [Pascal, *Bull. soc. chim.*, **35**, 1131 (1925); Boullé, *Compt. rend.*, **200**, 658 (1935); and Partridge, Hicks, and Smith, *J. Am. Chem. Soc.*, **63**, 454 (1941)]. The most reliable of these studies seems to be that of Partridge, Hicks, and Smith, who used thermal and X-ray methods. First they measured the temperature changes when NaH_2PO_4 was heated at a steady rate. The temperature-time curve showed only one definite break, which occurred at about 500°. Then they heated fresh samples of NaH_2PO_4 at various temperatures below fusion for forty hours—one sample for each temperature. X-ray powder pictures of the samples showed three distinct crystal forms, III, II, and I. The results are expressed diagrammatically as follows:

$$\begin{tikzcd}
\mathrm{NaPO_3III} \arrow[r, "400\text{–}425^\circ"] & \mathrm{NaPO_3II} \arrow[r, "475\text{–}500^\circ"] & \mathrm{NaPO_3I} \arrow[r, "625^\circ"] & \text{melt} \arrow[d, "\text{rapid cooling}"] \\
& & & \text{glass} \arrow[ull, "\text{reheating to } 300^\circ \text{ or above}"] \arrow[ul, "\text{chiefly}"']
\end{tikzcd}$$

The method of cooling was not made clear, but presumably the samples were allowed to cool in air. The transformations appear in general to be irreversible. The authors made no attempt to identify the forms found with distinct polymers. The $NaPO_3III$ and $NaPO_3II$ are insoluble and correspond to Maddrell's salt. The two forms could be either two polymers or different crystalline modifications of the same polymer. On the other hand, it may well be that the structure of the crystal is continuous and there are no distinct molecular units. It will be recalled, for example, that the stable crystalline modification of phosphorus pentoxide has a continuous structure while the less stable α form has a molecular structure. Owing to its low solubility (less than 0.1 g/liter at 15°), nothing is known of the chemical properties of Maddrell's salt. It is also insoluble in solutions of pyrophosphates and hexametaphosphates.

The $NaPO_3I$ is soluble and corresponds to Knorre's salt or trimetaphosphate. Its melting point was found to be 625°; other values given in the literature range from 600° to 640°. If the melt is allowed to cool slowly, crystals of $NaPO_3I$ form. If, however, the melt is quenched, a glass without ordered structure is obtained. This is Graham's salt; it is soluble in water and is usually referred to as the hexametaphosphate. Heating the quenched melt for some time at 300° or above causes it to crystallize chiefly to $NaPO_3I$ (trimetaphosphate), but partly to $NaPO_3II$ (Maddrell's salt), especially at the lower temperatures.

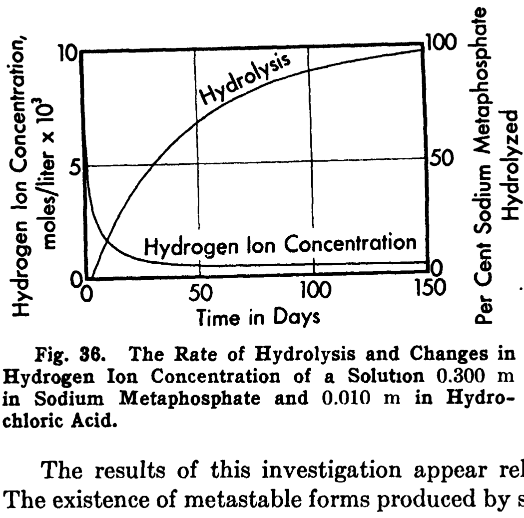


Fig. 36. The Rate of Hydrolysis and Changes in Hydrogen Ion Concentration of a Solution 0.300 m in Sodium Metaphosphate and 0.010 m in Hydrochloric Acid.

The results of this investigation appear reliable as far as they go. The existence of metastable forms produced by short heating, or of forms stable only in a very restricted temperature range, is by no means excluded, however. It was mentioned that the investigators are not in perfect agreement. They do all agree that first an insoluble salt and then, above about 500°, a soluble salt is formed. Boullé [*Compt. rend.*, **200,** 658 (1935)] obtained about the same transition points as did Partridge, Hicks, and Smith, but he reported the unexpected result that $NaPO_3I$ and $NaPO_3III$ have the same crystal structure.

Pascal [*Bull. soc. chem.*, **35,** 1131 (1925)] quenched the sodium metaphosphate from the desired temperature by plunging it into mercury. He then determined the conductance and freezing-point depressions in solutions of the salts. His results are summarized by the reaction scheme

$$NaH_2PO_4 \xrightarrow[250^\circ]{} \text{"}Na_2P_2O_6\text{"} \xrightarrow[505^\circ]{} Na_3P_3O_9 \rightleftharpoons Na_4P_4O_{12} \underset{607^\circ}{\rightleftharpoons} Na_6P_6O_{18}$$

This diagram agrees fairly well with that given previously except for the reversible formation of the tetrametaphosphate just below the melting point. Pascal's "$Na_2P_2O_6$" is insoluble and corresponds to Maddrell's salt, for which no formula has been established. The tetrametaphosphate could not be isolated in a pure state owing to the reversible nature of its formation. Evidence for its preparation under other conditions is given in a later paragraph.

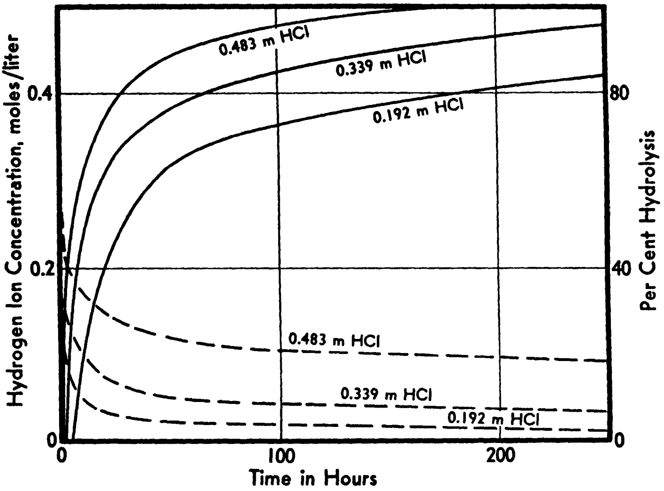


Fig. 37. The Rate of Hydrolysis and Change in Hydrogen Ion Concentration in Solutions 0.500 m in Sodium Metaphosphate Containing the Indicated Concentrations of Hydrochloric Acid. Solid lines represent hydrolysis; dashed lines, hydrogen ion concentration.

From the results given above, it would appear that the salt prepared by Beans and Kiehl and called by them the "monometaphosphate" was in reality practically pure trimetaphosphate, a conclusion supported somewhat by the freezing-point lowerings. However, they report also that their salt gave a precipitate with lead nitrate, a reaction more characteristic of the tetra- and hexa- metaphosphates than of the trimetaphosphate. This fact may indicate the presence of a considerable amount of hexametaphosphate; it should be pointed out, however, that the lead salt of trimetaphosphate is only moderately soluble and

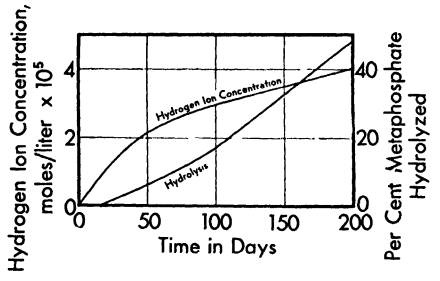


Fig. 38. The Rate of Hydrolysis and Change in Hydrogen Ion Concentration of a 0.300 m Sodium Metaphosphate Solution.

would give a precipitate in concentrated solution. The lack of any quantitative solubility data presents a considerable handicap in studying the metaphosphates.

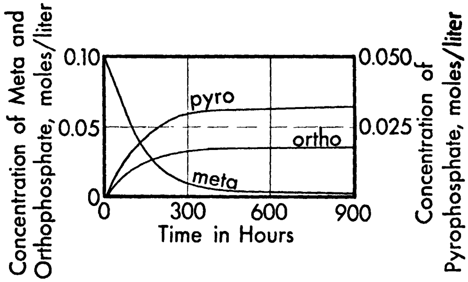


Fig. 39. The Rate of Hydrolysis of a Solution 0.100 m in Sodium Metaphosphate and 0.500 m in Sodium Hydroxide at 75° C.

Dilute acid solutions of the metaphosphates hydrolyze over a period of several weeks at room temperature to orthophosphoric acid, H_3PO_4. Hydrolysis is more rapid at higher temperatures. Rather careful measurements of the rate at 45° were made by Beans and Kiehl [*J. Am. Chem. Soc.*, **49**, 1878 (1927)] with the salt which they prepared and which is probably the trimetaphosphate; the results of some of their experiments are shown graphically in Figs. 36, 37, and 38. A mixture, 0.500 f in $NaPO_3$ and 0.483 m in HCl, is 50% hydrolyzed in 6.17 hours at 45°; when the HCl is 0.192 m, 25 hours are required for 50% hydrolysis. The reaction is complicated by the fact that pyrophosphoric acid is formed as an intermediate, and hydrogen ion is a catalyst.

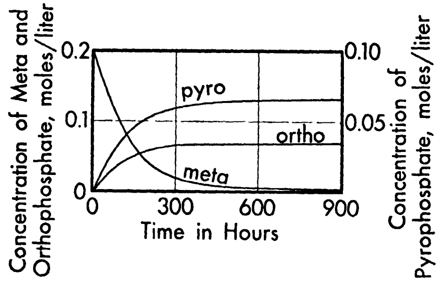


Fig. 40. The Rate of Hydrolysis of a Solution 0.200 m in Sodium Metaphosphate and 0.500 m in Sodium Hydroxide at 75° C.

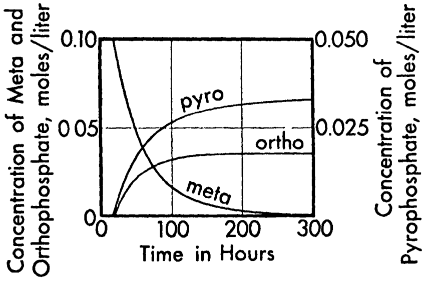


Fig. 41. The Rate of Hydrolysis of a Solution 0.100 m in Sodium Metaphosphate and 2.00 m in Sodium Hydroxide at 75° C.

In alkaline solution and at around 75°, the sodium trimetaphosphate prepared by Kiehl and his co-workers hydrolyzes according to the equation

$$(NaPO_3)_3 + 2H_2O = Na_2H_2P_2O_7 + NaH_2PO_4$$

The analytical method used to determine the amounts of meta-, ortho-, and pyrophosphate depended at one stage on the fact that zinc acetate in acetic acid solution will give a precipitate with pyrophosphate but not with meta- or orthophosphate, if these be present at concentrations not greater than 0.1 m. Some idea of the rate of the hydrolyses can be gathered from the following representative results at 75° of Kiehl and Coats [*J. Am. Chem. Soc.*, **49,** 2180 (1927)], and from Figs. 39, 40, and 41.

$NaPO_3$* Conc.	NaOH Conc	Per Cent Hydrolyzed to Pyro	Per Cent Hydrolized to Ortho	Time (hours)
0.10 f.	0.500 m.	30.5	16.7	89.5
"	"	64.0	34.3	713 5
.200	.500	27.8	16.7	84.
"	"	65.7	33.8	1298.
.100	2 00	27.0	20.0	45.
"	"	65.4	34.4	380.

* Probably $Na_3P_3O_9$.

The reaction is approximately first-order with respect to metaphosphate, and hydroxyl ion is a catalyst. A mechanism for the reaction has not been suggested. Titration curves made using sodium trimetaphosphate prepared by the method of Beans and Kiehl show that all three hydrogens in trimetaphosphoric acid ionize freely. The curves are indistinguishable from those of sodium chloride [Rudy and Schlosser, *Ber.*, **73,** 484 (1940)].

Sodium trimetaphosphate or Knorre's salt is also readily prepared by heating a molten mixture of Na_2HPO_4 (3 parts) and NH_4NO_3 (1 part) at about 330° for six hours [Knorre, *Z. anorg. Chem.*, **24,** 369 (1900)]. The salt prepared in this way has been shown to give the same X-ray powder spectrum as the salt prepared by heating pure NaH_2PO_4 at temperatures between 500° and 600° [Boullé, *Compt. rend.*, **200,** 658 (1935)]. Sodium trimetaphosphate may be purified from other metaphosphates by precipitating the latter as lead salts in dilute aqueous solution. Pure sodium trimetaphosphate is not hydroscopic. It is easily soluble in water and it does not give precipitates on addition of silver nitrate, lead nitrate, barium, or calcium chloride. The formula is supported by conductivity measurements and by the freezing-point lowerings, of which the most reliable are those of Nylèn [*Z. anorg. Chem.*, **229,** 30 (1936)]. He obtained the accompanying data. The molecular weight corresponding to complete ionization is 76.5. It is generally agreed that the trimetaphosphate is the best-established individual chemical specie in the metaphosphate system.

KNORRE'S SALT

g/100 g H_2O	$-\Delta T$	Molecular Weight
0.076	0.018°	78.5
.098	.023	79.3
.182	.040	84.8
.195	.043	84.4
.323	.066	91.0

Copper tetrametaphosphate is prepared by adding powdered CuO to a slight (5%) excess of orthophosphoric acid in a platinum vessel. The mixture is stirred thoroughly and allowed to stand until the mass is a clear blue throughout. Then it is heated slowly on a water bath and later on a sand bath. The temperature should not exceed about 450°. The preparation is finished as soon as the excess metaphosphoric acid begins to be evolved as a white vapor. The resulting mass is powdered and extracted with water; the insoluble copper tetrametaphosphate remains. Continued digestion of the salt with H_2S gives the free acid. Various salts can be prepared from the acid; the sodium salt is easily soluble. No precipitate is obtained with $AgNO_3$ or with $Co\,(NH_3)_6Cl_3$, but albumin is coagulated. Doubtful support for the formula $(NaPO_3)_4$ is given by Bonneman [*Compt. rend.*, **204**, 865 (1937)], who made cryoscopic measurements in fused $Na_2SO_4{\cdot}10H_2O$, and found a molecular weight of 418. The conductivities also supported the formula given. The X-ray powder spectrum was clear and entirely distinct from that of Knorre's salt. If $(NaPO_3)_4$ is heated at 375° for two hours, the X-ray lines characteristic of Knorre's salt appear; on heating 12 hours at 500°, the salt is converted entirely into Knorre's salt. If the compound is fused and quenched, Graham's salt results.

Graham's salt, or sodium hexametaphosphate, is prepared by fusing a sodium metaphosphate at about 650° and then quenching the melt. No other method of preparation seems to have been used. For a homogeneous product it is important to hold the melt at 650–700° for at least an hour to get complete dehydration and then to cool it very rapidly—preferably in thin sheets. The product obtained is hydroscopic and readily soluble in water; the solubility is 973.2 g/liter H_2O at 20° and 1744 g/liter H_2O at 80° [Bronnikov, *J. Applied Chem.* (U.S.S.R.) **12**, 1287 (1939)]. It produces precipitates with lead nitrate and benzidine; with Fe^{++} the soluble complex $Na_3FeP_6O_{18}$ is readily formed. Albumin is coagulated rapidly. The evidence offered for the formula $Na_6P_6O_{18}$ rests on conductance measurements [Tammann, *J. prakt. Chem.*, **45**, 463 (1892)], freezing-point determinations, and the dubious preparation of a salt $Ag_5NaP_6O_{18}$ [Rose, *Pogg. Ann.*, **76**, 1 (1849)]. Representative examples of the freezing-point lowerings obtained [Jawein and Thillot, *Ber.*, **22**, 655 (1889)] are shown here; the first column of the table shows the amounts of sodium hexametaphosphate dissolved in 100 g of water. The formula weight of $Na_6P_6O_{18}$ is 612. No reliable conclusions can be drawn from data for such large concentrations of highly charged ions.

g/100 g H_2O	$-\Delta T$	Molecular Weight
8.48	0.400°	389
10.08	.460	407

The true justification for calling Graham's salt a hexametaphosphate lies in the fact that its properties are different from the known lower polymers, and the next reasonable member of the series would be the hexapolymer. Actually, it is not at all certain that Graham's salt is a single chemical species. A recent investigation at Upsala showed that a technically "pure" sodium hexametaphosphate contained 26% of a highly polymerized substance which could be ultracentrafuged to give a well-defined sedimentary boundary [Lamm and Malmgren, *Z. anorg. Chem.*, **245**, 103 (1940)]. The presence of a variable amount of highly polymerized material in the different metaphosphates investigated would account for much of the confusion in the literature.

Solutions of carefully prepared Graham's salt are slightly acid (*p*H 6.2), owing probably to small amounts of $Na_2H_2P_2O_7$. The strength of the acid $(HPO_3)_6$ has been a matter of some dispute. Salih [*Bull. Soc. Chim.*, **3**, 1391 (1936)] decomposed lead hexametaphosphate with H_2S and titrated the free acid, using a conductivity method. His results indicated that four of the hydrogens ionize freely. Treadwell and Leutwyler [*Helv. Chim. Acta*, **20**, 931 (1937); **21**, 1450 (1938)] made *p*H titration curves of the acid and reported that two hydrogens ionize strongly but the remaining four are weak. Still more recently Partridge [*Dual Service News*, Hall Lab., Pittsburgh, 1937] and Rudy and Schlosser [*Ber.*, **73**, 484 (1940)] have made titration curves which indicate that all six hydrogens ionize freely, and that pure solutions of sodium hexametaphosphate should be neutral. This result appears to be the most reliable one. It is a striking fact that in all the phosphorus acids there is one rather freely ionizable hydrogen for each phosphorus atom; additional hydrogens are very weakly ionized.

The purer commercial samples of hexametaphosphate contain from 9 to 16% $Na_2H_2P_2O_7$ resulting from incomplete dehydration, and consequently they give solutions of *p*H between 5.5 and 6.4. Other commercial mixtures contain from 4 to 6% sodium carbonate or bicarbonate, as well as some $Na_4P_2O_7$ (up to 19%), and give alkaline solutions.

The commercial importance of hexametaphosphate is due largely to the fact that it forms a soluble complex with calcium ion $Na_2Ca_2P_6O_{18}$, and it may, therefore, be used to soften water and remove scale from boilers [Thomson, *Analyst*, **61**, 320 (1936); Andress and Würst, *Z. anorg. Chem.*, **237**, 113 (1938)]. If a solution of calcium ion is added gradually to one of $Na_6P_6O_{18}$, no precipitate will form until all the hexametaphosphate is converted to the complex; the addition of excess calcium ion results in the formation of the white, insoluble $Ca_3P_6O_{18}$. Complexes are also formed with barium, strontium, and magnesium. Portland cement is decomposed by solutions of $Na_6P_6O_{18}$, the calcium present being extensively dissolved.

It has also been discovered that exceedingly minute amounts (0.5 to 4 p.p.m.) of sodium hexametaphosphate in water greatly increase the stability of supersaturated solutions, notably of carbonate [Reitemeier and Buehrer, *J. Phys. Chem.*, **44**, 535 (1940)]. Similar amounts greatly inhibit the corrosion of metals by water. Both of these qualities are of extreme importance in water treatment [Schwartz and Munter, *Ind. Eng. Chem.*, **34**, 32 (1942)]. Calcium metaphosphate is coming into use as a fertilizer. The Tennessee Valley Authority manufactured over 24,000 tons in the four years 1937–1941 by a process of oxidizing phosphorus to P_4O_{10} and then passing the vapor over phosphate rock at 1000°C. Ninety-eight per cent of the oxide combines with the $Ca_3(PO_4)_2$ in the rock to produce a good quality of metaphosphate [Copson, Pole, and Baskerville, *Ind. Eng. Chem.*, **34**, 26 (1942)].

The stability of solutions of $Na_6P_6O_{18}$ is of considerable importance, but no very satisfactory investigation of it has been made. Germain [*Chim. et Ind.* **35**, 22 (1936)] has published some semi-qualitative investigations on the rate of hydrolysis made with 1% solutions of commercial salts containing, on the average, 12% of $Na_2H_2P_2O_7$. Hexametaphosphate was determined by its ability to form a complex with barium; other metaphosphates do not form barium complexes of great stability. Germain's results are expressed in grams of P_2O_5 per liter of 1% solution in Table 54 on the opposite page.

The pyro- and orthophosphate were determined by acidimetric titration using a series of indicators. The measurements are valuable in that they show the variation in complex-forming power with time under various conditions, but the analytical methods were inadequate to establish the nature or the exact amount of the decomposition products. With the better methods now available [Jones, *Ind. Eng. Chem. Anal. Ed.*, **14**, 536 (1942)], a more thorough study could be made.

In addition to the insoluble Maddrell salt, other insoluble metaphosphates have been reported and are known as the Kurrol salts. These salts are prepared by heating Na_2HPO_4 at various temperatures below fusion [Pascal, *Bull. soc. chim.*, **35**, 1131 (1924); *Compt. rend.*, **178**, 1541 (1924)]. Another method consists in the prolonged fusion and a slow crystallization of sodium hexametaphosphate. The preparation is capricious, and many investigators have been unable to obtain such salts. Pascal states that the Kurrol salts are crystalline and melt at 809° to give a liquid distinct from the hexametaphosphate melt. They are insoluble in water but are soluble in solutions of pyrophosphates and hexametaphosphates to give highly viscous and apparently colloidal solutions. From variations in viscosity of different preparations, Pascal concluded that there were three distinct Kurrol salts.

Although the existence of the sodium salts is disputed, it is agreed that the potassium salts do exist. On heating K_2HPO_4 to 170°, a soluble

TABLE 54

THE RATE OF HYDROLYSIS OF 1% $Na_6P_6O_{18}$ SOLUTIONS

(Concentrations are in grams of P_2O_5 per liter of solution.)

Temp. (°C)	Time in Days	*p*H	Hexameta-phosphate	Other Meta-phosphates	Pyrophos-phate	Ortho-phosphate
25	0	6.2	5.45	0.38	1.	0.07
	1		5.33	.53	.89	.15
	9		5.22	.57	.88	.23
50-60	0	6 2	5.45	.42	.96	07
	2		5.22	.36	.94	.38
	4		1.78	3.19	.88	1 05
	8		.23	4.17	.54	1 95
	Time in Hours					
70-80	0	6.2	5.33	.53	.89	.15
	2		4.85	.67	.93	.45
	6		3.32	1 51	1.01	1.06
	0	6.2	5.45	.42	.96	.07
	2		5.33	.40	1.02	.15
	6		4.50	.74	.99	.67
100	0	2.3 (H_2SO_4)	5.86		1.04	0
	2	1.1	0		.27	6 63
	0	8 4	5.45	.41	.97	07
	3	7.3	1.78	2.63	.83	1.66
	6	6.9	.23	3.54	.95	2.18
	8	6.9	0	3.72	.77	2.41
	14	6 9	0	3.24	.35	3.31

potassium trimetaphosphate is produced; no salt corresponding to Maddrell's salt is known. On heating to above 320°, a Kurrol salt is formed which melts at 838°. Experiments of Lamm and Malmgren [*Z. anorg. Chem.*, **245**, 103 (1940)] illustrate the behavior of the substance. They heated K_2HPO_4 to a red glow for twenty minutes, sintering it to a hard white mass. The insoluble material was powdered and treated with two equivalents of concentrated sodium chloride solution. The powder gradually flowed together into an extraordinarily viscous, elastic mass. The potassium is partly replaced by sodium, and most of the substance becomes soluble. Addition of more sodium chloride reprecipitates the viscous mass. The chloride was removed by kneading the mass with alcohol. A 1% solution was neutral and had a viscosity five times that of water. After the high viscosity was diminished by addition of an electrolyte, the substance behaved as a normal, high-molecular-weight compound. The original value of the mean molecular weight in dilute HCl was 20,000. In dilute (less than 0.3 m) NaCNS solutions, the polymer proved stable and its mean molecular weight was found to be from 100,000 to 140,000. The polymer hydrolyzes more rapidly in hydrochloric acid than in NaOH solution.

The polyphosphates

Investigations of the polyphosphates, $Na_{n+2}P_nO_{3n+1}$, have shown that in addition to the pyrophosphate, $Na_4P_2O_7$, only $Na_5P_3O_{10}$ certainly exists. This salt is formed by melting mixtures of NaH_2PO_4 and Na_2HPO_4 or $Na_6P_6O_{18}$ and $Na_4P_2O_7$. The pure salt $Na_5P_3O_{10}$ is soluble in water and, like the hexametaphosphate, forms a soluble complex with calcium, $Na_3CaP_3O_{10}$. Aqueous solutions of $Na_5P_2O_{10}$ hydrolyze to orthophosphate only slowly (after weeks) at room temperature; on the addition of acid, the hydrolysis is much more rapid [Andress and Würst, *Z. anorg. Chem.*, **237,** 113 (1938)].

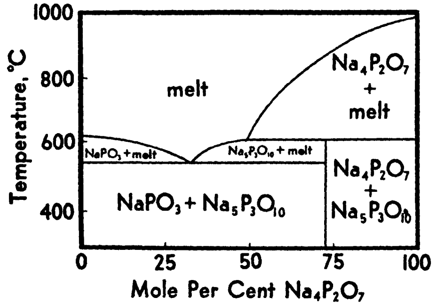


Fig. 42. The Phase Diagram of the System $NaPO_3$-$Na_4P_2O_7$.

Partridge, Hicks, and Smith [*J. Am. Chem. Soc.*, **63,** 454, (1941)] have made a thermal and X-ray study of the polyphosphate system $NaPO_3$-$Na_4P_2O_7$. Their results, which are in excellent agreement with the conclusions of Andress and Würst [*loc. cit.*], are summarized in the phase diagram, Fig. 42, taken from their paper.

In the acid $H_5P_3O_{10}$, three hydrogens ionized strongly and two much more weakly. The acid is somewhat stronger than pyrophosphoric acid [Rudy and Schlosser, *Ber.*, **73,** 484 (1940)].

Pyrophosphoric acid

This acid is formed as an intermediate in the hydrolysis of metaphosphoric acid, and when ordinary orthophosphoric acid is evaporated at elevated temperatures. Solutions of the pure acid are best obtained indirectly from its salts, for example, by igniting disodium hydrogen phosphate, Na_2HPO_4. A platinum dish should be used for the ignition, since hot phosphates will dissolve much silica from glass or porcelain vessels. The conditions under which the pyrophosphate is formed from dihydrogen phosphate, NaH_2PO_4, may be seen from the dissociation pressures of H_2O above two phase mixtures of the two salts as measured by Kiehl and Wallace [*J. Am. Chem. Soc.*, **49,** 375 (1927)].

$$2NaH_2PO_4(s) = Na_2H_2P_2O_7(s) + H_2O(g) \qquad (A)$$

$$nNa_2H_2P_2O_7(s) = 2(NaPO_3)_n(s) + nH_2O \qquad (B)$$

Temp. (°C)	(A) p_{H_2O} (in mm)	(B) p_{H_2O} (in mm)	Temp. (°C)	(A) p_{H_2O} (in mm)	(B) p_{H_2O} (in mm)
100	6.7	—	200	—	85
120	36.1	—	240	—	296
140	194.	—	260	—	517
150	750.	—	280	—	760
170	—	11			

It is presumed that no solid solutions were formed by the ortho and pyrophosphates, although this was not proved.

Sodium pyrophosphate dissolves readily in water to form stable solutions at room temperature. If to the hot solutions concentrated copper sulfate is added, a precipitate of copper pyrophosphate forms which may be washed and treated in aqueous suspension with excess hydrogen sulfide to obtain a solution of pyrophosphoric acid. The precipitate of CuS is filtered off, and the excess hydrogen sulfide is removed by passing a stream of air through the solution. Heating the solutions of $H_4P_2O_7$ brings about their hydrolysis to orthophosphoric acid. By careful evaporation solid $H_4P_2O_7$ is obtainable; it melts at about 61°.

Although neutral or alkaline solutions of pyrophosphates are quite stable with respect to conversion into orthophosphate, acid solutions, even at room temperature, hydrolyze slowly to the common orthophosphoric acid, H_3PO_4.

$$H_4P_2O_7 + H_2O = 2H_3PO_4$$

The rate of this hydrolysis has been repeatedly studied. Abbott [*J. Am. Chem. Soc.*, **31,** 763 (1909)] showed, by conductivity measurements, that, approximately at least,

$$-\frac{d(\Sigma H_4P_2O_7)}{dt} = k(H^+)(\Sigma H_4P_2O_7)$$

and for a 0.05 formal solution at 100°, $k' = 1.53$; at the same concentration, but at 75°, $k' = 0.127$ where the k' are numbers directly proportional to the k. The factor of proportionality is not known; it includes the undetermined ratio of the conductance of the solutions to the concentration of H^+. The extent of the hydrolysis with time is more conveniently seen from a table prepared by Abbott (upper table, page 226). From these results it may be estimated that at 45° about 40 hours would be required for 50% hydrolysis of a solution initially 0.05 formal.

A closer insight into the mechanism of pyrophosphoric acid hydrolysis was obtained by Pessel [*Monatshefte*, **43,** 601 (1923); see Kailan, *Z. phys. Chem.*, **160A,** 301 (1932)] and by Muus [*Z. phys. Chem.*, **159A,** 268 (1932)]. They studied the reaction in the presence of excess hydrochloric acid. In the experiments of Muus ($\Sigma H_4P_2O_7$) was 8.07×10^{-4} m and the concentration of HCl was many times greater than this, namely, about 0.03 to 0.25 m. Many of the experiments were carried out in KCl solutions, so that the ionic strength remained practically constant. A colorimetric method of analysis was used; to 5 cc samples of the solutions were added 2 cc of ammonium molybdate solution (500 cc of 5% solution plus 200 cc 5 n H_2SO_4), 1 cc of 20% Na_2SO_3, and 1 cc of ½% hydrochinon. With orthophosphate, but not with pyrophosphate, a blue-colored solution was produced which may be compared with standards made up under like conditions. Muus found, just as did Abbott, that

Initial Conc. $H_4P_2O_7$ (moles/l soln.)	Per Cent Hydrolyzed	Time (minutes)
0.0125 at 75°	25	88
	50	220
	75	470
0.05 at 75°.	25	52
	50	135
	75	290
0.05 at 100°....	25	5
	50	12.5
	75	27

$$-\frac{d(\Sigma H_4P_2O_7)}{dt} = k'(H^+)(\Sigma H_4P_2O_7)$$

and he showed, moreover, that the rate equation is, more precisely,

$$-\frac{d(\Sigma H_4P_2O_7)}{dt} = k(H^+)(H_3P_2O_7^-)$$

since the ion $H_3P_2O_7^-$ is present initially in greatest and most constant concentration in solutions of varying acidity. This result suggests that $H_4P_2O_7$ is the reactive substance. When the time is expressed in hours, k has the values shown in the table. Expressed otherwise, we may say that when the concentration of hydrogen ion is 1 m, 50% of the pyrophosphoric acid in a solution will have hydrolyzed in 16 hours at 40° and in 172 hours at 20°. Essentially the same results were obtained by Pessel.

KCl (conc. m/l)	Temp. (°C)	$k \times 10^3$
1.0	40	44.2
0.0	40	65.0
1.0	20	3.97
0.0	20	6 5

So far we have followed the hydrolysis of meta- and pyrophosphoric acids to orthophosphoric acid in dilute solution. If one begins with the dilute ortho acid and evaporates the solution until the temperature reaches about 149°, a syrupy, concentrated orthophosphoric acid results. From 150 to 160° only a little water is lost; but if the temperature is raised to 212–213°, evaporation proceeds slowly with formation of a solution consisting principally of pyrophosphoric acid. Evaporation at 255–260° produces almost pure pyro acid, but evaporation at 290–300° brings about the formation of some metaphosphoric acids; further concentration at still higher temperatures leads to increased amounts of the metaphosphoric acids. Clearly, the hydrolytic reactions are reversible, but practically nothing is known about the equilibrium concentrations of the various acids in their concentrated solutions.

The ionization of pyrophosphoric acid is discussed in the following section on orthophosphates.

Orthophosphates

Solutions of pure orthophosphoric acid are best prepared by the action of nitric acid (specific gravity, 1.2) on pure white phosphorus. Pure orthophosphoric acid is a white solid which melts at 42.30° to a liquid showing a strong tendency to supercool. The heat of fusion is 2520 cal/mole. There is a solid semihydrate $2H_3PO_4 \cdot H_2O$ which melts at 29.35°. Only the strongest and most reactive reducing agents have any effect on pure phosphoric acid. With metallic sodium, a sodium phosphide is formed. In general, the reduction reactions have no especial interest at present.

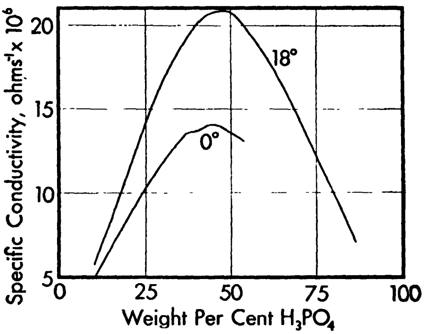


Fig. 43. The Specific Conductivity of Phosphoric Acid Solutions at 0° and 18° C.

Since the solution of phosphorus pentoxide in water does not lead directly to orthophosphoric acid, the energy quantities obtained with it and water are variable, and a reliable value for the heat of solution to give the ortho acid is not available. By oxidizing phosphorus with bromine solutions, an accurate value for the heat of formation of H_3PO_4 in dilute solutions has been obtained. Determination of the heats of dilution of pure orthophosphoric acid offer no especial difficulty.

The importance of accurate thermodynamic knowledge of phosphates and phosphoric acids is obvious. These substances play a vital part in soil fertility, and it is essential that applied fertilizers have *all* the properties conducive to a continuously productive agriculture. The following brief discussion indicates the nature of our present information on some relevant compounds.

The heat and free energy of ionization of pyro- and orthophosphoric acids have been repeatedly investigated and by a variety of methods.

In the case of orthophosphoric acid, Pitzer [*J. Am. Chem. Soc.*, **59,** 2365 (1937)] has determined heats of ionization and has made a critical selection of the ionization constants. The constants for pyrophosphoric acid are known with fair accuracy.

THE IONIZATION OF ORTHO AND PYROPHOSPHORIC ACIDS

H_3PO_4	ΔH°_{298}	ΔF°_{298}	$-\Delta S^\circ_{298}$	K
First hydrogen.	−1880	2898	16.0	7.5×10^{-3}
Second hydrogen.....	800	9830	30.3	6.2×10^{-8}
Third hydrogen...........	3000	16,300	43.	10^{-13}

$H_4P_2O_7$, $K_1 = 0.14$, $K_2 = 0.011$, $K_3 = 2.1 \times 10^{-7}$, $K_4 = 4.06 \times 10^{-10}$ at 18°
$H_4P_2O_7$, in
1 n KCl at 18°, $K_2 = 0.027$, $K_3 = 3 \times 10^{-6}$

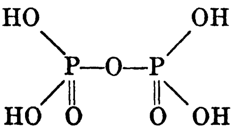
Careful determinations of the first and second ionization constants of H_3PO_4 by means of electromotive force measurements have been made at a variety of temperatures by Nims [*J. Am. Chem. Soc.*, **56,** 1110 (1934); **55,** 1946 (1933)]. If K_1 is expressed as $K_1 = 10^{-pK}$, then, for dilute solutions, the following are reliable values of pK_1 and K_2.

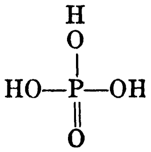
IONIZATION CONSTANTS OF H_3PO_4 AT VARIOUS TEMPERATURES

t (°C)	pK_1	t (°C)	$K_2 \times 10^8$
0.3	2.048	20	6.056
12.5	2.076	30	6.349
25.	2.124	40	6.471
37.5	2.185		
50.	2.260		

$$\log_{10} K_1 = -2.0304 - 5 \times 10^{-5}(t + 18)^2$$
$$\Delta H^\circ_T = 4.58 \times 10^{-4} T^2(T - 255.1)$$

When comparison is made between the ionization constants of the ortho and pyro acids, it is seen that the latter is much the stronger. This behavior is observed in other oxyacids containing one and more than one nuclear acidic element. Thus, $HCr_2O_7^-$($K_2 = 2.3 \times 10^{-2}$) is stronger than $HCrO_4^-$($K_2 = 3.2 \times 10^{-7}$). This fact is probably to be explained, roughly, by the changes resulting from oxygen-bond formation, the effect being to increase the distance and hence reduce the interaction





between an un-ionized hydrogen and the oxygens attached to the other phosphorus atom.

Of interest are the partial vapor pressures of water above orthophosphoric acid. These are given for several temperatures and concentrations in the following table and Fig. 44 [Kablukov and Zagwosol, *Z. anorg. Chem.*, **224**, 315 (1935)].

TABLE 55
THE PARTIAL VAPOR PRESSURES OF WATER IN mm Hg ABOVE ORTHOPHOSPHORIC ACID SOLUTIONS

Concentration (moles H_3PO_4/ 1000 g water)	25°	40°	60°	80°	Concentration Weight Per Cent
0.00	23.756	55.324	149.38	355.1	00.0
0.612	23.45	54.42	147.18	349 41	5.66
1.08	23.21	53.93	145.63	347.89	9.57
3.03	—	50.82	139.76	330.94	22.16
6.05	20.70	46.54	128.76	300.91	36.67
11.80	16.50	35.40	96.96	235.07	54.13
17.56	11.49	27.37	74.23	182.94	63.11
46.46	3.95	8.66	27.37	73.13	81.46
68.30	2.93	4.82	14.30	—	87.11

These data may be used to calculate the partial molal heat of vaporization of the water from solutions of any concentration. The directly determined values for the 40% acid are $\Delta H^{\circ}_{350} = 10{,}100$ cal and $\Delta H^{\circ}_{374.6} = 9850$ cal, and for the 50% acid $\Delta H^{\circ}_{351.7} = 10{,}300$ cal and $\Delta H^{\circ}_{376.4} = 10{,}100$ cal per mole of water vaporized.

In principle, the vapor-pressure results may be used to calculate the activities of the acid over the whole range of concentrations, but this has not yet been done.

It is evident that even the 90% orthophosphoric acid cannot be used as an effective drying agent, since at 25° the partial vapor pressure of water is already 1.69 mm. The affinity of P_2O_5 for water is very much greater than that of 90% phosphoric acid, the vapor pressure of water in equilibrium with a P_2O_5-$(HPO_2)_n$ mixture being less than 10^{-5} mm.

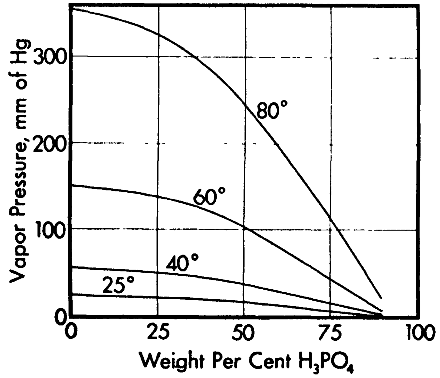


Fig. 44. The Partial Vapor Pressure of Water above Phosphoric Acid Solutions.

When water is added to a phosphoric acid solution, its temperature rises, and the increase in energy is known as the *heat of dilution.* Rumelin [*Z. phys. Chem.*, **58,** 460 (1907)] determined the heats of dilution, dE/dn, when a small amount of water was added to large amounts of solution. His results are as follows:

Composition of Solution—Weight Per Cent H_3PO_4	Energy Change per Mole Water Added, dE/dn (cal/mole)	Specific Heat of Solution (cal/gram)	Temperature (°C)
32.72	33.5	0.697	17.65
28.18	19.9	.776	17.63
21.50	12.3	.813	17.16
15.36	8.2	.834	17.50

The heats of solution of crystalline H_3PO_4 in n moles of water are [Bichowsky and Rossini, *Thermochemistry*]:

n	$-\Delta H^\circ_{291}$ (cal)	n	$-\Delta H^\circ_{291}$ (cal)
400	2790	20	2320
200	2730	9	1890
100	2650	3	680
50	2550		

The densities of orthophosphoric acid solutions are comparable to those of sulfuric acid at the same weight per cent concentrations, as the following specific gravities at 20°/4° show.

Per Cent Acid	H_3PO_4	H_2SO_4	Per Cent Acid	H_3PO_4	H_2SO_4
1	1.0038	1.0051	60	1.426	1.4983
10	1.0532	1.0661	80	1.633	1.7272
20	1.1134	1.1394	90	1.746	1.8144
40	1.254	1.3028	100	1.870	1.8305

All of the hydrogens in ortho- and pyrophosphoric acid are replaceable. This fact is illustrated by the following well-established salts. The corresponding ammonium salts are also known. Because of the weakness of both the acid and the base, the tri- and diammonium compounds hydrolyze extensively in aqueous solution.

Salt	Solubility in Water (g/100 g water)		
$NaH_3P_2O_7$	62.7 (18°)[a]		
$Na_2H_2P_2O_7 \cdot 6H_2O$	14.95 (18°)[a]		
$Na_3HP_2O_7 \cdot 6H_2O$	28.17 (18°)[a]		
$Na_4P_2O_7 \cdot 10H_2O$	8.14 (25°)		
"	17.45 (50°)		
	0°	25°	100°
$NaH_2PO_4 \cdot 2H_2O$	57.86 (0.1°)	94.63	246.56 (NaH_2PO_4 at 99.1°)
$Na_2HPO_4 \cdot 12H_2O$	1.67 (−0.5°)	12	102.15 (Na_2HPO_4 at 99.77°)
$Na_3PO_4 \cdot 12H_2O$	1.5	15.5	108

[a] g/100g soln.

The following are representative of the variety of insoluble salts of orthophosphoric acid:

$Mg_3(PO_4)_2 \cdot 4$, 8, and $22H_2O$	$Co_3(PO_4)_2 \cdot 8H_2O$
$MgHPO_4 \cdot 7H_2O$	$Ni_3(PO_4)_2 \cdot 7H_2O$
$Mg(H_2PO_4)_2 \cdot 2H_2O$	$Cu_3(PO_4)_2 \cdot 3H_2O$
$NH_4MgPO_4 \cdot 6H_2O$	$Pb_3(PO_4)_2\ 4H_2O$
$Zn_3(PO_4)_2 \cdot 4H_2O$	$Fe_3(PO_4)_2 \cdot 8H_2O$
$ZnHPO_4 \cdot 2H_2O$	$FeHPO_4 \cdot H_2O$
$Zn(H_2PO_4)_2 \cdot H_2O$	$Fe(H_2PO_4)_2 \cdot 2H_2O$
$AlPO_4 \cdot 4\frac{1}{2}H_2O$	$FePO_4 \cdot 4H_2O$

In addition to these, a number of phosphates occur naturally, for example, $[Ca(Ca_3(PO_4)_2)_3]F_2$ (apatite). The phosphorus in these may be replaced by As or V, as in $[Pb(Pb_3(AsO_4)_2)_3]F_2$ (Mimetisite) and $[Pb(Pb_3(VO_4)_2)_3]Cl_2$.

The addition of excess phosphoric acid to solutions of ferric ion leads to the formation of the soluble complexes [Weinland and Ensgraber, *Z. anorg. Chem.*, **340,** 84 (1913)] $H_3[Fe(PO_4)_2]$ and $H_6[Fe(PO_4)_3]$.

Sodium and ammonium phosphates have found extensive application as fertilizers, the ammonium salts furnishing both available phosphorus and nitrogen to the soil. The sodium salts are much used in aqueous solution as buffers for the maintenance of practically constant concentrations of hydrogen ion during titrations with strong acids or bases. For this purpose moderately large concentrations are necessary, since, for example, in the relation

$$(H^+) = K_2 \frac{(H_2PO_4^-)}{(HPO_4^=)}$$

the (H^+) will remain constant on the addition of a strong acid only if the ratio ($H_2PO_4^-$)/($HPO_4^=$) is not greatly altered, *i.e.*, if neither the numerator nor the denominator is changed by more than a per cent or so. When ($H_2PO_4^-$) = ($HPO_4^=$) ≈ 1 m, one has a buffer solution in which (H^+) = 10^{-7} nearly; that is, the solution is practically neutral and will remain so if comparatively small amounts of a strong acid or base are added to it.

The compound $NaNH_4HPO_4$, known as microcosmic salt, is used in bead tests for metal oxides; the mixed phosphates formed by the fusion (on a platinum loop) of the microcosmic salt with the metal oxide are often distinctively colored. $CoNaPO_4$, for example, is blue.

The thermodynamic constants for the phosphoric acids and phosphates are for the most part only approximately known. For the formation of H_3PO_4 in dilute solution from H_2, P (red), and O_2, $\Delta H^\circ = -302{,}000$ cal and $\Delta F^\circ_{298} = -270{,}000$ cal [Latimer, *Oxidation Potentials*]. Latimer also gives estimates of the standard potentials of the important couples at 25°. Most of these oxidation potentials are quite large and are in accord with the long-known fact that the phosphorus compounds in the lower oxidation states are strong or powerful reducing agents.

Reaction	E° (in volts)
$H_2O + H_3PO_3 = H_3PO_4 + 2H^+ + 2E^-$	0.20
$3OH^- + HPO_3^= = PO_4^{\equiv} + 2H_2O + 2E^-$	1.05
$2H_2O + H_4P_2O_6 = 2H_3PO_4 + 2H^+ + 2E^-$	0.8
$2H_3PO_3 = H_4P_2O_6 + 2H^+ + 2E^-$	0.4
$H_2O + H_3PO_2 = H_2PO_3 + 2H^+ + 2E^-$	0.59
$3OH^- + H_2PO_2^- = HPO_3^= + 2H_2O + 2E^-$	1.65
$2H_2O + P = H_3PO_2 + H^+ + E^-$	0.29
$2OH^- + P = H_2PO_2^- + E^-$	1.82

Of particular interest from the thermodynamic point of view is the hydrolysis of phosphorus in water.

$$4P\ (\text{red}) + 6H_2O = PH_3(g) + 3H_3PO_2, \qquad \Delta F^\circ_{298} = -17{,}000 \text{ cal}$$

This large negative value of ΔF°_{298} shows that the hydrolysis is, at equilibrium, practically complete with $K \approx 10^{13}$; that is, the pressure of phosphine in equilibrium with P (red) and a molal solution of hypophosphorus acid would be enormous, $\approx 10^{13}$ atm, and beyond our ability to measure. This reaction does not, therefore, provide an avenue of approach to the accurate evaluation of the free energies of phosphorus compounds.

We shall conclude this section on phosphoric acids with a table of some of their characteristic reactions with precipitants. Of the precipitants for the orthophosphates, ammonium molybdate in nitric acid solution is the most interesting. The yellow compound formed is a complex with a phosphorus nucleus, $(NH_4)_3H_4[P(Mo_2O_7)_6]\cdot H_2O$; it is only slightly soluble in water, 0.03 g/100 g H_2O at 15°, but the free acid, $H_7[P(Mo_2O_7)_6]\cdot 10H_2O$, is soluble. The acid is heptabasic, and the normal salts of guanidine, $CN_3H_6^+$, silver, and mercury have been prepared. The corresponding tungsten compounds are known, $M_7[P(W_2O_7)_6]$, and a mixed vanadium molybdenum complex as well, $R_7[P(V_2O_6)_3(Mo_2O_7)_3]$. Phosphomolybdic acids in which all of the phosphate oxygens are not replaced by the pyromolybdate radical are known, for example [Rosenheim and Janecke, *Z. anorg. Chem.*, **100**, 304 (1917)],

$$H_7[P(Mo_2O_7)_6], \qquad H_7[PO(Mo_2O_7)_5], \qquad H_7[PO_2(Mo_2O_7)_4]$$

Compounds like the phosphomolybdic acids are known as *heteropolyacids;* a large number of them are known to have nuclei other than phosphorus—for example, hydrogen, arsenic, boron, thorium, silicon, tin, cerium, titanium, zirconium, tellurium, iron, cobalt, copper, manganese, and nickel. All of the saturated heteropolyacids contain six addenda of the type $Mo_2O_7^=$ or $MoO_4^=$.

Normal zirconium phosphate is insoluble even in concentrated sulfuric acid.

TABLE 56
REACTIONS OF PHOSPHORIC ACIDS IN AQUEOUS SOLUTION

Reagent	Orthophosphoric Acid	Pyrophosphoric Acid	Metaphosphoric Acid
$AgNO_3$	Yellow Ag_3PO_4	White crystl. $Ag_4P_2O_7$	White gelatinous ppt.
$BaCl_2$	No ppt. in acid, white $Ba_3(PO_4)_2$ in alkaline soln.	No ppt. in acid; $Ba_2P_2O_7$ in alkali	White ppt.
$Zn(Ac)_2$[a]	No ppt.	White $Zn_2P_2O_7$	No ppt.
$(NH_4)_2MoO_4$ in HNO_3	Yellow ppt.	No ppt.	No ppt.
$Co(NH_3)_6Cl_3$	No immediate ppt.	Reddish-yellow ppt.	No immediate ppt.
Al^{+++}	Ppt. soluble in HAc	Ppt. insoluble in HAc	Ppt. insoluble in HAc
Cr^{+++}	Ppt. soluble in HAc	Ppt. insoluble in HAc	Ppt. insoluble in HAc
Bi salts in alkali	No ppt.	No ppt.	White ppt.
Albumin	No ppt.	No ppt.	White ppt.

[a] HAc = acetic acid, CH_3COOH.

It will be realized that the reactions listed under metaphosphoric acid are subject to some reservations as a consequence of the existence of several polymers of this acid. In this connection it may be said that a thorough experimental investigation of the metaphosphoric acids and their salts would be of utmost scientific value; no other element exists in a single-valence stage in such a variety of acids having so many puzzling properties as does phosphorus.

CHAPTER 7

Phosphorus Halides and Oxyhalides. Phosphine

The Phosphorus Halides and Oxyhalides

Preparation

White phosphorus combines readily and often violently with the halogens to form compounds of the type PX_3, PX_5, or P_2X_4. With red phosphorus, the reactions are somewhat less violent but lead to the same products. In all cases further purification is necessary to obtain a product free from a halide higher or lower than that desired. This fact is exemplified by the procedures found necessary by Baxter, Moore, and Boylston [*J. Am. Chem. Soc.*, **34,** 259 (1912)] for the preparation of PBr_3 for atomic-weight determinations. Their method of purification involved a series of fractional distillations of both the phosphorus and bromine used as well as of the product, PBr_3. Phosphorus trichloride can also be prepared in a high state of purity in a similar way.

Ordinarily the chlorides and bromides are prepared, as indicated, by allowing the elements to come together in an appropriate vessel. The iodides are best made by mixing solutions of white phosphorus and iodine in carbon disulfide and then removing the solvent by evaporation. The fluorides are most conveniently prepared by treating the chlorides directly with liquid arsenic trifluoride, AsF_3, resublimed antimony trifluoride SbF_3 (Swarts' reaction), or calcium fluoride. The liquid AsF_3 is dropped from a funnel directly onto the PCl_3 or PCl_5; the reaction proceeds smoothly at room temperature, or a few degrees above, and becomes more rapid with time, owing to the fact that at first the two immiscible liquids do not present much surface of contact but, as more $AsCl_3$ forms, the original two-phase liquid mixture becomes a single phase containing in solution both of the reactants. The volatility of the AsF_3 (b.p., 58°) makes necessary its removal from the reaction products by a fractional distillation.

$$PCl_3 + AsF_3 = PF_3(g) + AsCl_3$$

The trifluoride may also be formed by warming a mixture of ZnF_2 and PBr_3, or by heating copper phosphide with lead fluoride. When resublimed antimony trifluoride is used, it is added in the powdered form to the liquid to be fluorinated; antimony pentachloride and SbF_3Cl_2 act as catalysts in this and other fluorination reactions using antimony trifluoride, and it is conveniently obtained by partially chlorinating the SbF_3 with chlorine until about ten per cent of it is converted to SbF_3Cl_2. In some cases it is desirable to reflux the liquid chloride to be fluorinated in such a way that its vapors circulate through the antimony trifluoride. Calcium fluoride promises to become a convenient and cheap fluorinating agent, although the best conditions for its use have not yet been worked out; the vapors of the chloride or bromide to be fluorinated are simply passed through a heated tube containing the CaF_2. These reactions lead not only to the phosphorus fluoride alone, but, under proper conditions, to the mixed halides as well. Thus, PF_3Cl_2 and the corresponding bromides may be prepared through the Swarts and the calcium fluoride fluorinating reactions; $POFCl_2$ and POF_2Cl may be prepared in the same manner [Booth, *vide infra*].

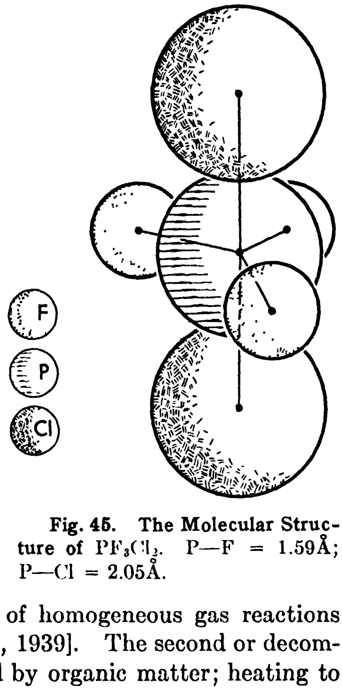


Fig. 45. The Molecular Structure of PF_3Cl_2. P—F = 1.59Å; P—Cl = 2.05Å.

Phosphorus trifluoride reacts with chlorine and bromine with moderate rapidity at room temperature to form PF_3Cl_2 and PF_3Br_2, respectively, and these compounds are decomposed by gentle to moderate heating into phosphorus pentafluoride and the pentachloride or pentabromide.

$$PF_3(g) + Cl_2(g) = PF_3Cl_2(l)$$
$$5PF_3Cl_2(g) = 3PF_5(g) + 2PCl_5(s)$$

The first reaction is measurably slow in the gas phase and quite rapid if PF_3 is caused to react with liquid chlorine; the gas-phase reaction, taking place to considerable extent on the walls of the reaction vessel, does not belong to the class of homogeneous gas reactions [Norton Wilson, Thesis, Cal. Inst. Tech., 1939]. The second or decomposition reaction appears to be catalyzed by organic matter; heating to 100° or less suffices for the decomposition in the absence of catalysts.

An interesting haloid, the isocyanate, $P(NCO)_3$, of trivalent phosphorus has been prepared recently by Forbes and Anderson [*J. Am. Chem. Soc.*, **62,** 761 (1940)]. The compound results from a warm mixture of PCl_3 (90 g), AgNCO (230 g), and benzene (300 cc); purification of the product is effected through several distillations. Phosphorus triisocyanate is a colorless liquid with b.p. = 169.3° and m.p. = −2°; the vapor pressures are given by $\log_{10} p_{mm} = 8.7455 - 2595/T$, and $\Delta H_{vap.} =$ 11,900 cal. Its density is 1.439 at 20°. The liquid will stand for two weeks without change, but on cooling to −20°, melting at −2°, and then standing at room temperature for three days, it becomes a solid, melting at about 80° or even 95° if repeatedly melted.

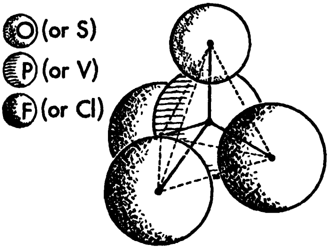


Fig. 46. The Molecular Structures of $VOCl_3$, $POCl_3$, POF_3, PSF_3, $PSCl_3$.

	V—O	P—O	P—S	P—X	V—X	∠X—P—X	∠X—V—X
$VOCl_3$	1.56Å				2.12Å		111°
$POCl_3$		1.58Å		2.02Å		106°	
POF_3		1.56		1.52		107	
PSF_3			1 85Å	1.51		99.5	
$PSCl_3$			1.95	2.01		107	

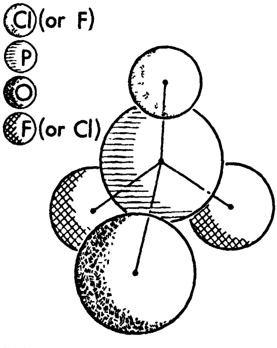


Fig. 47. The Molecular Structures of POF_2Cl and $POFCl_2$.

	P—O	P—F	P—Cl	∠F—P—Cl = ∠F—P—F = ∠Cl—P—Cl
POF_2Cl	1.55Å	1.51Å	2.01Å	106°
$POFCl_2$	1 54	1.50	1.94	106

All of the phosphorus halides with the exception of PF_3 hydrolyze very rapidly with water, and advantage is taken of this fact in the preparation of the oxyhalides. Thus, with a little water the reaction

$$PCl_5(s) + H_2O(l) = POCl_3(l) + 2HCl(g)$$

takes place. With excess water orthophosphoric acid, H_3PO_4, is formed. $POCl_3$ may be prepared on a larger scale by passing chlorine over $Ca_3(PO_4)_2$ and charcoal at 750° [Rozhdestvenskii, *Trans. State Inst. Applied Chem.* (*U S.S.R.*), **20,** 47 (1934)]. The oxychloride, in turn, may be converted to the trichloride by passing it over coal at red heat. Both $POCl_3$ and $POBr_3$ result with good yields when PCl_5 or PBr_3 are mixed with P_2O_5. Phosphorus oxyfluoride is formed by direct hydrolysis of PF_5 with little water or by the direct action of HF (g or l) on P_2O_5. When cryolite, Na_3AlF_6, is heated in a brass tube with P_2O_5, POF_3 is formed.

Of the phosphorus fluorides, the trifluoride is most readily prepared pure; and since it neither attacks glass nor hydrolyzes rapidly in moist air, it is not difficult to store if reasonable precautions are taken. It does hydrolyze if passed directly into water or alkali.

An interesting series of fluophosphoric acids has been prepared and studied by Lange [*Ber.*, **62,** 1054, 782 (1929) *et ante*]. They may be regarded as derivatives of metaphosphoric acid.

HPF_6	HPO_2F_2	H_2PO_3F
Hydrofluophosphoric acid	Difluophosphoric acid	Monofluophosphoric acid

The preparation consists in heating phosphorus pentoxide at 135° with ammonium fluoride, in adding the pentoxide to 40% hydrofluoric acid, or in hydrolyzing incompletely POF_3 with cold, dilute alkali. Both HPF_6 and HPO_2F_2 form relatively insoluble salts with Nitron, $C_6H_5NNCN(C_6H_5)CHNC_6H_5$, a monoacidic base, and these salts serve as a starting point for the preparation of others. Solutions of the alkali salts of HPF_6 and HPO_2F_2 are neutral to methyl orange and phenolphthalein, hence the acids are strong. The salts of HPF_6 resist hydrolysis, and boiling with strong alkali decomposes them only slowly; hydrolysis is more rapid in strong acids. Dilute alkali will hydrolyze the salts of HPO_2F_2 to those of H_2PO_3F, and hot strong acids will hydrolyze the latter to phosphoric and hydrofluoric acids, but dilute alkali will not. In many ways HPO_2F_2 resembles perchloric acid, especially in the solubility of its salts. Solutions of the acid salt $KHPO_3F$ are acid to methyl orange while those of K_2PO_3F are neutral to this indicator.

Properties

Of special interest in recent years have been the mixed halides of phosphorus, and their preparation and purification are due, for the most part, to Booth and his co-workers [*J. Am. Chem. Soc.*, **61,** 3120 (1939) *et ante*]. The importance of these volatile mixed halides results from the fact that the influence of the different halogens on the bond angles

TABLE 57

THE PHYSICAL PROPERTIES OF THE PHOSPHORUS HALIDES AND OXYHALIDES

Substance	Boiling Point (°C)	Melting Point (°C)	Heat of Vaporization, ΔH° (cal)	Critical Temp. and Pressure (atm)	Standard Entropy of Gas, S°_{298} (cal/deg/mole)	Heat of Formation, $-\Delta H^\circ_{298}$ (cal)	Bond Angle, X—P—X	Interatomic Distances (Å), P—X[b]
PF_3	−101.15	−151.5	3490	−2.05 (42.69)	64.13	—	104°	1.52
PF_2Cl	−47.3	−164.8	4200	89.17 (44.61)	—	—	—	—
$PFCl_2$	13.85	−144.0	5950	189.84 (49.3)	—	—	102°	2.02 1.55
PCl_3	74.2	−111.8	7278	—	74.49	69,120(g) 76,900(l)	101°	2.00
PF_2Br	−16.1	−133.8	5721	—	—	—	—	—
$PFBr_2$	78.4	−115.0	7624	—	—	—	—	—
PBr_3	175.3	−40	—	—	83.11	45,000(l)	100°	2.23
PF_5	−75	−83	—	—	—	—	[a]	1.57[a]
PF_3Cl_2	10	−8	—	—	—	—	[a]	P—F,[a] 1.59 P—Cl, 2.05
PCl_5	160 (sublimes)	148?	15,500	—	84.3	106,500(s)	—	P—F, 2.04 P—Cl, 2.11[c]
PF_3Br_2	—	−20	—	—	—	—	—	—
PBr_5	Dec.	<100	—	—	—	60,600(s)	—	—
P_2I_4	Dec.	124.5	—	—	—	19,800	—	—
PI_3	—	61.0	—	—	—	10,900	98°	—
POF_3	−39.8	−39.4	5030	73.3 (41.8)	—	—	107°	P—F, 1.52 P—O, 1.56
$POCl_3$	105.1	1.25	8200	—	77.59	138,400(g) 147,100(l) 150,300(s)	106°	P—Cl, 2.02 P—O, 1.58

TABLE 57 (*Cont.*)

Substance	Boiling Point (°C)	Melting Point (°C)	Heat of Vaporization, $\Delta H°$ (cal)	Critical Temp. and Pressure (atm)	Standard Entropy of Gas, $S°_{298}$ (cal/deg/mole)	Heat of Formation, $-\Delta H°_{298}$ (cal)	Bond Angle, X—P—X	Interatomic Distances (Å), P—X[b]
$POBr_3$	189.5	56	–	–	–	106,900(s)	–	–
$POFCl_2$	52.9	−80.1	7400	–	–	–	106°	P—O, 1.54 P—F, 1.50 P—Cl, 1.94
POF_2Cl	3.1	−96.4	6090	150.6 (43.4)	–	–	106°	P—O, 1.55 P—F, 1.51 P—Cl, 2.01
$POFBr_2$	110.1	−117.2	7520	–	–			–
POF_2Br	30.5	−84.8	7093	–	–	–	–	–
$PSCl_3$	125	−35	–	–	79.34	–	107°	P—Cl, 2.01 P—S, 1.95
$PSCl_2F$	64.7	−96.0	6863	–	–	–	–	–
$PSClF_2$	6.3	−155.2	5703	166 (40.9)	–	–	–	–
PSF_3	−52.3	−148.8	4684	72.8 (37.7)	–	–	–	P—F, 1.51 P—S, 1.85
$PSBr_3$	206	37	–	–	–	–	–	–

---

[a] These molecules are trigonal bipyramids.

[b] The P—X distance depends only on X and not on the compound. Thus P—Cl is essentially constant for all phosphorus halides containing chlorine.

[c] In the trigonal bipyramid, two P—Cl distances appear to be 2.11 Å and the other three are 2.04 Å. (Pauling, *The Nature of the Chemical Bond*, p. 103.)

which they make with the phosphorus atom may be readily determined by electron-diffraction experiments. Reference to the table and the accompanying figures will show the interesting fact that the bond angle is almost invariant to the substitution of the halogens by each other. Moreover, the P—X distances in this class of substances are dependent mainly on X and not on the particular compound [see Brockway, *Rev. Modern Phys.*, **8**, 231 (1936); Pauling, *The Nature of the Chemical Bond*].

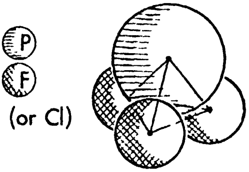


Fig. 48. **The Molecular Structure of** PF_3 and PCl_3. P—F = 1.52Å; P—Cl = 2.00Å; ∠F—P—F = 104°; ∠Cl—P—Cl = 101°.

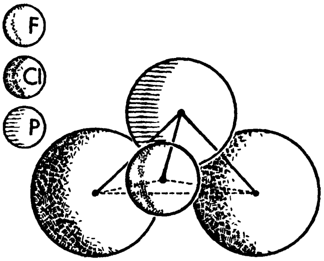


Fig. 49. **The Molecular Structure** of $PFCl_2$. P—F = 1.55Å; P—Cl = 2.02Å; ∠Cl—P—Cl = 102°.

There are few measurably reversible reactions to be found among phosphorus compounds; two exceptions are the pentabromide and pentachloride, which decompose reversibly into the trihalide and the halogen.

TABLE 58

MOLECULAR CONSTANTS FOR SOME PHOSPHORUS COMPOUNDS

(Frequencies are in cm^{-1}.)

	$\omega_1 \parallel$	$\delta_1 \parallel$	$\omega \perp$	$\delta_1 \perp$	$\omega_2 \parallel$	$\delta_2 \perp$	P—X Å	P—O Å	Shape, bond angle
PH_3	2320	970	2430	1118			1.42		Pyramidal, 93°
PF_3	890	531	840	486			1 52		Do, 104°
PCl_3	511	257	480	190			2 00		Do, 101°
PBr_3	400	162	380	116			2.23		Do, 100°
$POCl_3$	1290	267	581	193	486	337	2.02	1.56	Cl—P—Cl 106°
$PSCl_3$	748	245	539	169	430	382	2.01	1 94	Cl—P—Cl 107°
Degeneracy	1	1	2	2	1	2			

The decomposition of the pentachloride has been repeatedly studied but not by precision methods [see Anderson and Yost, *J. Chem. Phys.*, **4**, 529 (1936); Fischer and Jubermann, *Z. anorg. Chem.*, **235**, 337 (1938)].

$$PCl_5(s) = PCl_5(g)$$
$$\Delta H^\circ_T = 30{,}763 - 38.144T, \quad \Delta F^\circ_T = 30{,}763 + 87.83T \log_{10} T - 302.36T$$
$$PCl_5(g) = PCl_3(g) + Cl_2(g)$$
$$\Delta H^\circ_T = 20{,}000 + 3.473T, \quad \Delta F^\circ_T = 20{,}000 - 7.99T \log_{10} T - 17.27T$$

These empirical formulas do not represent the measurements in a completely satisfactory manner; the following table presents the experimental values of the equilibrium constants together with the values of ΔH°_0 calculated by Dr. D. P. Stevenson [*J. Chem. Phys.*, **9**, 403 (1941)] on the assumption that the two unobserved vibrational frequencies are 450 and 600 cm^{-1}, respectively, the observed frequencies in the Raman effect being 100, 190 (2), 271 (2), 392, 449 (2), and 495 (2) cm^{-1}. The molecule is a trigonal bipyramid with equatorial P—Cl distances of 2.03 Å and axial P—Cl distances of 2.12 Å (see Fig. 50).

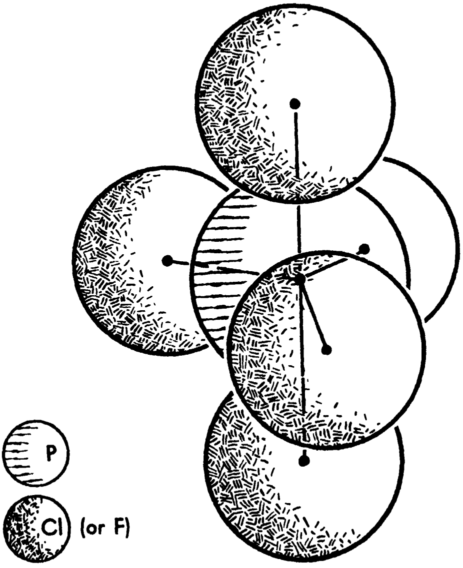


Fig. 50. The Molecular Structure of PCl_5 and PF_5. P—Cl equatorial = 2.03Å; P—Cl axial = 2.12Å; P—F (average) = 1.57Å.

$$PCl_3(g) + Cl_2(g) = PCl_5(g)$$
$$K_{atm} = \frac{P_{PCl_5}}{P_{PCl_3}P_{Cl_2}}$$

Temp. (°K)	K_{atm}	ΔH°_0 (kcal.)	Temp. (°K)	K_{atm}	ΔH°_0 (kcal.)
422.6	122.63	21.44	473.1	5.816	21.20
430.3	67.96	21.35	502.2	1.752	21.35
442.7	45.22	21.61	556.0	0.2048	21.31
454.0	15.52	21.22	623.0	0.0234	21.21
464.5	8.88	21.20			

It is evident that the two assumed frequencies, which were selected by trial, lead to satisfactorily constant values of ΔH°_0.

In Table 58 are collected the vibrational frequencies and interatomic distances for a few of the phosphorus halides for which the data are reliably known. The entropies (Table 57) and the free-energy functions for these molecules have been calculated by Yost and Stevenson [*J. Chem. Phys.*, **9**, 403 (1941)].

The phosphorous halides combine with many substances to form addition or complex compounds, and in organic chemistry they find application as chlorinating and brominating agents.

All of the pentavalent halides hydrolyze readily even in moist air, but the trivalent compounds vary in this respect. Phosphine is not very reactive toward water or moisture (it may inflame in air); PF_3 likewise hydrolyzes only slowly in moist air, more rapidly in water, and quite rapidly in alkali. PF_2Cl hydrolyzes slowly in air; $PFCl_2$ does so more rapidly but does not fume; PF_2Br and $PFBr_2$ both fume in moist air; PCl_3 and PBr_3 are both fuming liquids at room temperature. Evidently the reactivity of this group of compounds toward water decreases as the sum of the atomic numbers of the three attached halogens decreases.

All of the mixed trihalides of phosphorus show a tendency to decompose spontaneously into the simpler ones. For example,

$$3PF_2Br = 2PF_3 + PBr_3$$

and this reaction takes place extensively in a few days [Booth and Frary, *J. Am. Chem. Soc.*, **61**, 2934 (1939)]; $PFBr_2$ decomposes much more slowly (into PF_3 and PBr_3), and the corresponding fluochlorides are decomposed extensively only at higher temperatures, 200° or higher. The reaction

$$PF_3 + PCl_3 = PFCl_2 + PF_2Cl$$

is reversible and at 400° results in about 30% conversion into the mixed halides; the mixed halides will decompose according to the equation at the same temperature. No rate or equilibrium data for these reactions exist. When the mixed trihalides are treated with chlorine or bromine, unstable liquid or solid mixed pentahalides are formed.

Phosphorus iodides

Two iodides of phosphorus are well established, namely, PI_3 and P_2I_4. These are prepared by mixing carbon disulfide solutions of white phosphorus and iodine in proper proportions, partially evaporating the mixture, and then cooling the resulting solution until the crystals separate. If the atomic proportions of P and I are as one is to three, PI_3 (dark red) will result; if as one is to two, P_2I_4 (clear red needles) is formed [Germann and Traxler, *J. Am. Chem. Soc.*, **49**, 307 (1927)]. The carbon disulfide solutions of PI_3 are dark red. Mixtures intended for the preparation of P_2I_4 are at first brown and then a beautiful, transparent red in color. PI_3 is also formed when a solution of iodine in carbon bisulfide is treated with an excess of P (red); the solution that results when reaction is complete is dark red in color. It is possible that the equilibrium P_2I_4 (in CS_2) + I_2 (in CS_2) = $2PI_3$ (in CS_2) exists, although no measurements of it are recorded. The tri-iodide is somewhat unstable at higher temperatures; its vapor density at moderate temperatures corresponds to PI_3, but little is known about the nature of the decomposition reaction. PI_3 (m.p., 61°) hydrolyzes in moist air and water to form phosphorous and hydriodic acids. The di-iodide, P_2I_4 (m.p., 124.5°), is somewhat unstable on heating and is decomposed into PI_3 and I_2. When P_2I_4 is added to water, a number of compounds are formed in proportions depending on the temperature of the water; at 0°, HI, H_3PO_2, H_3PO_3, H_3PO_4, PH_3, and $P_{12}H_6$ are formed. The immediate oxidation of an alkaline solution of P_2I_4 with 30% H_2O_2 leads to a conversion of 24% of the phosphorus to hypophosphate ion, $P_2O_6^{≣}$ [Kolitowski, *Roczniki Chem.*, **15**, 29 (1935)].

TABLE 59

THE RATE OF REACTION BETWEEN PHOSPHORUS AND IODINE IN CARBON TETRACHLORIDE SOLUTION AT 15°

(Concentrations are expressed in moles per liter of solution, and the rates $-R$ in millimoles of iodine per liter per minute.)

Initial (P_4) = 0.0084; initial (I_2) = 0.00400.

(P_4) × 10^3	(I_2) × 10^3	$-R$	(P_4) × 10^3	(I_2) × 10^3	$-R$
39.9	3.50	0.25	39.4	1.75	0.005
39.8	3.00	.10	39.4	1.50	.008
39.7	2.75	.046	39.3	1 25	.014
39.6	2.50	.029	39.2	1.00	.020
39.6	2.25	.014	39.2	.75	.029
39.5	2.00	.007			

Initial (I_2) = 0.00250

(P_4) × 10^3	$-R$, at (I_2) = 2.00 × 10^{-3}m	(P_4) × 10^3	$-R$, at (I_2) = 1.50 × 10^{-3}m
4.9	0.036 × 10^{-1}	4.7	0.023 × 10^{-1}
9.9	.098	9.7	.062
14.9	.36	14.7	.23
19.9	.94	19.7	.60
24.9	2.0	24.7	1.25
29.9	3.5	29.7	2.0
34.9	6.0	34.7	2.8

$$\frac{R[(I_2) = 2 \times 10^{-3}]}{R[(I_2) = 1.5 \times 10^{-3}]} \approx 1.6$$

The reaction between white phosphorus and iodine in dry carbon tetrachloride solution is slow, and its rate has been investigated and found to be a complicated function of the concentrations of the reactants [Wyllie, Ritchie, and Ludlam, *J. Chem. Soc.*, 583 (1940)]. In all experiments made, the proportions of phosphorus and iodine corresponded to 2P + 4I or to (2 + x)P + 4I, so that at most P_2I_4 would be eventually formed and not any PI_3. It was established at the beginning of the study that when reaction is complete in a mixture containing 2P + 4I, no free iodine is present. The reaction mixtures were analyzed for iodine by a colorimetric comparison method. In the table on page 243 are presented results for some of the representative experiments made by Wyllie, Ritchie, and Ludlam.

The rate of disappearance of iodine depends strongly on the concentration of phosphorus, especially when this is large, and much less strongly on the iodine concentration. Moreover, in a single run, the rate goes through a minimum, as is shown by the results in the first section of the table. These facts are in qualitative and approximate quantitative accord with the rate equation:

$$-\frac{d(I_2)}{dt} = \frac{4k_1(P_4)(I_2)^2}{(I_2) - b(P_4)}\left\{1 + \frac{k_1c(P_4)(I_2)}{(I_2) - b(P_4)}\right\}$$

When $k_1 = 10.0$, $b = 0.04$ and $c = 0.6$, and the rate is expressed in millimoles per liter per minute.

This rate equation, as Wyllie, Ritchie, and Ludlam point out, has only approximate validity and must be regarded as tentative, but it does reproduce the main features of the experimental results. A mechanism of the reaction which is in accord with the rate equation consists of the following set of reactions:

$$P_4 + I_2 = P_4I_2 \quad (1) \qquad P_2 + I_2 = P_2I_2 \quad (4)$$
$$P_4I_2 = P_2I_2 + P_2 \quad (2) \qquad P_2I_2 + I_2 = P_2I_4 \quad (5)$$
$$P_2I_2 + P_4 = P_4I_2 + P_2 \quad (3) \qquad P_2I_2 + P_2I_2 = P_2I_4 + P_2 \quad (6)$$

It is assumed further that a steady state obtains in which the concentrations of the intermediates P_4I_2, P_2I_2, and P_2 remain constant. From these considerations the rate equation given above may be derived with $b = 2k_3/k_5$, $c = 4k_6/k_5^2$. The assumption that all intermediates are a steady-state concentrations may not be correct, since the same values of *k*, *b*, and *c* do not suffice to reproduce the experimentally found rates during the whole period of a single experiment. Attention should be called to the fact that the mechanism is not inconsistent with the fact that small concentrations of iodine will act to catalyze the reaction in which phosphorus solutions are converted to red phosphorus. This reaction is doubtless one of polymerization, and one step in the process could be $P_4 + P_2 = P_6$, followed by similar reactions to attain the necessary degree of polymerization.

In the discussion, the phosphorus-iodine reaction has been considered taking place in a solution of dry carbon tetrachloride. The addition of small amounts of water and other substances catalyzes the reaction strongly; with water as a catalyst, the rate may be over a hundred times faster than that found for the dry carbon tetrachloride solutions.

Phosphine and the Phosphonium Halides

Phosphine

The formation of phosphine, PH_3, in a number of reactions involving the decomposition of phosphorus or its lower oxyacids has already been discussed. Its preparation is more conveniently carried out by carefully adding calcium phosphide, Ca_3P_2, to water or, for the purest product, by treating phosphonium iodide with alkali. The hydrolysis of calcium phosphide produces not only phosphine but the liquid diphosphine (hydrogen hemiphosphide), P_2H_4, the analogue of hydrazine, as well. The relative amounts of PH_3 and P_2H_4 produced depend on the composition of the calcium phosphide. Like ammonia, phosphine is also formed slowly by the direct combination of the gaseous elements; the yield increases with increase in pressure and decrease in temperature.

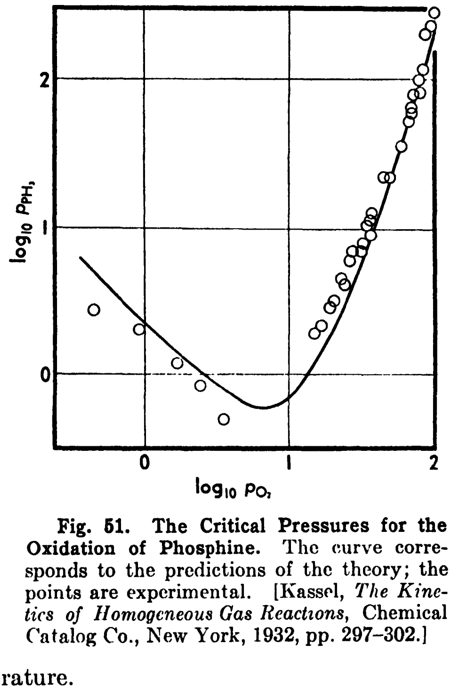


Fig. 51. The Critical Pressures for the Oxidation of Phosphine. The curve corresponds to the predictions of the theory; the points are experimental. [Kassel, *The Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co., New York, 1932, pp. 297–302.]

Phosphine is a colorless gas which, under certain conditions of pressure and temperature, will inflame spontaneously in oxygen. The gas from the hydrolysis of calcium phosphide inflames spontaneously in any proportion of air, and this effect is thought to be due to the presence of P_2H_4, since the latter is very reactive toward oxygen. Phosphine is only moderately soluble in water, 26 cc in 100 cc water at 17°, and it gradually decomposes in this solvent into phosphorus, hydrogen, and the

Temp. (°K)	$K_{atm} \times 10^{12}$
627	10
677	5.6
731	2.5
771	1.9

lower hydrides of phosphorus. Phosphonium hydroxide is a much weaker base than is ammonium hydroxide, but the ionization constant is not known. An unstable hydrate $PH_3 \cdot H_2O$ or PH_4OH is known.

The equilibrium reaction of formation of phosphine from the elements has been studied in a silver-lined bomb at high pressures and temperatures by Ipatiew and Frost [*Ber.*, **63,** 1104 (1930)]. Their results have been recalculated by Stevenson and Yost [*J. Chem. Phys.*, **9,** 403 (1941)], who have derived the equilibrium constants given on page 245 and the following free energies:

$$P_4(g) + 6H_2(g) = 4PH_3(g) \qquad K = \frac{P^4_{PH_3}}{P_{P_4}P^6_{H_2}}$$

$$\Delta H^\circ_0 = 1530 \text{ cal}$$

$$\Delta F^\circ_{298} = -18{,}370 \text{ cal}$$

$$P(w) + \tfrac{3}{2}H_2(g) = PH_3(g)$$

$$\Delta F^\circ_{298} = -3{,}140 \text{ cal}$$

The negative value of ΔF°_{298} shows that even at room temperature there is a moderately strong tendency for phosphine to form from solid white phosphorus and hydrogen; the reaction is immeasurably slow, however, and it is not until a temperature of over 300° is reached that appreciable amounts of phosphine are formed from P and H_2.

Measurements have been made of the low-temperature heat capacities of phosphine by Stephenson and Giauque [*J. Chem. Phys.*, **5,** 149 (1937)]; their results, together with other physical chemical properties, are presented in Table 60. Like ammonia, the phosphine molecule is pyramidal in shape with a H—P—H bond angle of 93°. In ammonia, the H—N—H bond angle is 109°. The P—H distance is 1.42 Å; the corresponding distance in ammonia is N—H = 1.01 Å [see Howard, *J. Chem. Phys.*, **3,** 207 (1935); Stevenson, *J. Chem. Phys.*, **8,** 225 (1940)].

TABLE 60
THE PHYSICAL PROPERTIES OF PHOSPHINE
Heat Capacity (cal/mole/deg)

Temp. (°K)	C_p, α	C_p, γ, β, δ, and liq.	Temp. (°K)	C_p, α	C_p, γ, β, δ, and liq.
15	0.96	1.56	80	—	12.06
20	1.79	2.46	90	—	11.15
25	2.66	3.85	100	—	11.21
30	3.56	6.23	110	—	11.28
35	4.48	10.90	120	—	11.37
40	5.38	9.77	130	—	11.53
45	6.31	10.32	140	—	14.75
50	—	10.78	170	—	14.44
60	—	11.42	185	—	14.49
70	—	11.79			

TABLE 60 (*Cont.*)
Heats of Transition, Fusion, and Vaporization
(cal/mole)

Temp. (°K)	ΔH° (cal)
30.29	19.6
49.43	185.7
88.10	115.8
139.35, m.p	270.4
185.38, b.p	3489.

Vapor pressures:

$$\text{Solid, } \delta, \log_{10} p_{cm} = -\frac{895.700}{T} + 6.86434;\ 129\text{–}139^\circ\text{K}$$

$$\text{Liquid, } \log_{10} p_{cm} = -\frac{1027.300}{T} - 0.0178530T + 0.000029135T^2 + 9.73075$$

In the gas equation $PV = RT + BP$, B in cc is accurately represented by the empirical equation [Long and Gulbransen, *J. Am. Chem. Soc.*, **58**, 203 (1936)]:

$$B_{cc} = 406.4 - \frac{1.0450 \times 10^5}{T} - \frac{3.02163 \times 10^7}{T^2} + \frac{1.3141 \times 10^{12}}{T^4} + \frac{2.2656 \times 10^{16}}{T^6}$$

Critical temp., $T_c = 324.1^\circ\text{K}$, $P_c = 64$ atm
Entropy:

$$S^\circ_{298}\ (\text{Exp.}) = 50.35\ \text{cal/deg}$$
$$S^\circ_{298}\ (\text{Spectr.}) = 50.5\ \text{cal/deg}$$

Specific gravity D **of liquid** PH_3 **at** T(°K):

$$D = 0.744 + 0.0005952(186.8 - T)$$

Surface tension γ **of liquid:**

Temp. (°C)	−105 9	−93.1
γ, dynes/cm	22.783	20.798

Decomposition rate of gaseous PH_3**:**

$$-\frac{dP_{PH_3}}{dt} = kP_{PH_3}$$

Temp. (°C)	310	440	512
k,* sec^{-1}	0.00021	.0025	.0081

* Surface or wall reaction; k varies strongly with nature and extent of surface of containing vessel.

Phosphine melts at 139.35°K under its own vapor pressure of 2.733 cm. There are four solid modifications: the first or α form is stable below a transition point at 49.43°K, and goes over into the second or β form at the transition point. By rapid cooling, the β form may be obtained below the normal α—β transition temperature. The third form, the γ, is observed with the supercooled β form below 30.29°K; at about 36°K the supercooled β form shows an abnormally high heat capacity over a small temperature range. The fourth form, δ, exists above a transition temperature of 88.10°K.

The low-temperature studies on the α and γ forms of phosphine have made possible a test of the third law of thermodynamics. In one form this law states that at 0°K the entropies of all allotropic modifications of a pure substance are equal. That this is true, for the α and γ forms of phosphine, is seen from the following calculation of molal entropy changes. If the entropies of the α and γ forms were not equal at 0°K, then the entropy changes from 0° to 49.43°K would not be equal for the two thermodynamic paths.

Process	α Form	γ (Supercooled β) Form
0–15°K, Debye function	0 338	0.495
15–30.29°, Heating	—	2.185
15–49.43°, Heating	4.041	—
Transition, γ–β, 19.6/30.29°	—	0.647
Transition, α–β, 185.7/49.43°	3.757	—
30.29–49.43°, Heating	—	4.800
$S^{\circ}_{49.43}$ (cal/deg)	8.14	8.13

Phosphonium and ammonium halides

When gaseous phosphine and hydrogen iodide are mixed, beautiful, colorless, tetragonal crystals of phosphonium iodide, PH_4I, are deposited. This compound is more conveniently prepared by first treating a carbon disulfide solution of white phosphorus (100 g) with iodine (175 g) and then evaporating the mixture—toward the end, in a stream of CO_2—to dryness. The dark-colored residue is treated portionwise with water (50 g); the resulting reaction leads to the formation and deposition of crystals of moderately volatile PH_4I on the walls of the flask and the attached condenser. Resublimation of the crystals leads to a purer and more beautiful product; fairly large crystals of PH_4I often appear in sealed tubes containing the compound if they are allowed to stand for several days or weeks at room temperature. The corresponding bromide and chloride are gases at room temperature and one atmosphere.

Phosphonium halides react with water, alkalis, or acids to form phosphine and the halogen acid.

$$PH_4I + aq = PH_3 + H^+ + I^-$$

Since phosphonium hydroxide is a very weak base, and since phosphine is only moderately soluble in water, 26 cc in 100 cc water at 17°, gaseous phosphine is evolved when phosphonium iodide is added to water alone. For the preparation of pure phosphine, it is preferable to use an alkali as a hydrolytic agent, since otherwise the liberated gas may not be wholly free from phosphonium iodide (PH_3 + HI). In the solid state phosphonium iodide is slowly attacked by air to give iodine and oxides of phosphorus. The volatility of phosphonium iodide, s.p. = 80°, makes possible the sublimation of the solid even at room temperature.

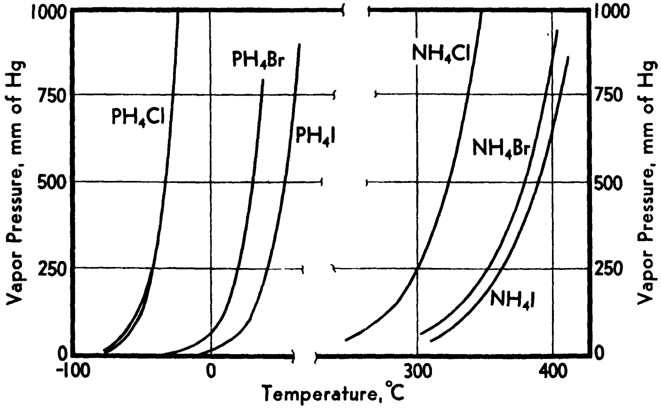


Fig. 52. The Vapor Pressures of Phosphonium and Ammonium Halides.

It is of interest at this point to compare some of the properties of the phosphonium and ammonium halides. The vapors of both are practically completely dissociated at ordinary pressures according to the reactions

$$PH_4X(s) = PH_3(g) + HX(g)$$
$$NH_4X(s) = NH_3(g) + HX(g)$$

One of the phosphonium halides, the chloride, exhibits a fairly uncommon phenomenon in that the vapor (hypercritical liquid) may be in equilibrium with the solid above the critical temperature. The same effect is shown by helium, the solid-vapor equilibrium being established at temperatures above which liquid-vapor equilibrium is possible. The pressure-temperature curves are shown for all but one of the phosphonium and ammonium halides in Figs. 52 and 53 [Smith and Calvert, *J. Am. Chem. Soc.*, **36**, 1363 (1914); Johnson, *J. Am. Chem. Soc.*, **34**, 877 (1912); Tammann, *Z. Electrochem.*, **8**, 158 (1902)]. The following table of physical properties of PH_4Cl shows its behavior in several respects; Fig. 53 exhibits the unusual phase relations.

Table 61

THE PHYSICAL PROPERTIES OF PHOSPHONIUM CHLORIDE

Melting point under own vapor pressure (°C)	28.5
Sublimation point (°C)	−28
Critical temperature (°C)	48.8–50.1
Critical pressure	74.2–75.0 atm
Heat of fusion at 28.5°	12,680 cal/mole

Change in molal volume, ΔV, on fusion under pressure at various temperatures:

Temp. (°C)	ΔV (cc/mole)
28.5	61.4*
40	51.5
50	45.5
60	40.9

* That these values are extraordinarily large may be seen by comparing with water, for which $\Delta V = 1.64$ cc/mole at 0°, and with naphthalene, for which $\Delta V = 18.7$ cc/mole at 80.1°.

The heat capacities of phosphonium iodide and the ammonium halides have been repeatedly investigated with the view of finding an explanation for what have come to be known as transitions of the second order or lambda-points. The molal heat capacity of $PH_4I(s)$ increases steadily and very nearly linearly from 11.97 cal/deg at −180° to 24.86 cal/deg at 10°; there are no discontinuities or unusual changes in the C_p, T curve in this temperature range. On the other hand, the ammoumni halides show marked changes in C_p in an interval of from 5 to 10°

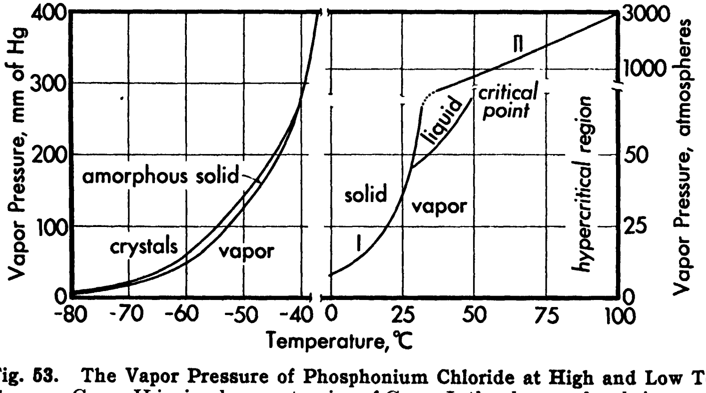


Fig. 53. The Vapor Pressure of Phosphonium Chloride at High and Low Temperatures. Curve II is simply an extension of Curve I; the change of scale is responsible for the apparent break.

in the temperature range from about -30 to $-43°$, the interval and the range depending on the salt. In Figs. 54 and 55 are shown the C_p versus T curves for $PH_4I(s)$ and several ammonium salts [Simon, von Simonson, and Ruheman, *Z. phys. Chem.*, **129**, 339 (1927); Crenshaw and Ritter, *Z. phys. Chem.*, **16B**, 143 (1932); Eucken, a review in *Z. Electrochem.*, **45**, 126 (1939)].

The lambda-point, that is, the temperature at which the heat capacities show a maximum, does not correspond to an ordinary isothermal transition such as is observed with rhombic-monoclinic sulfur or yellow-red mercuric iodide, but rather to one for which the heat of transition, ΔH, and the change in molal volume, ΔV, are quite small or zero. Liquid helium at 2.2°K exhibits a similar point, and some of its physical properties change rapidly or discontinuously in this neighborhood.

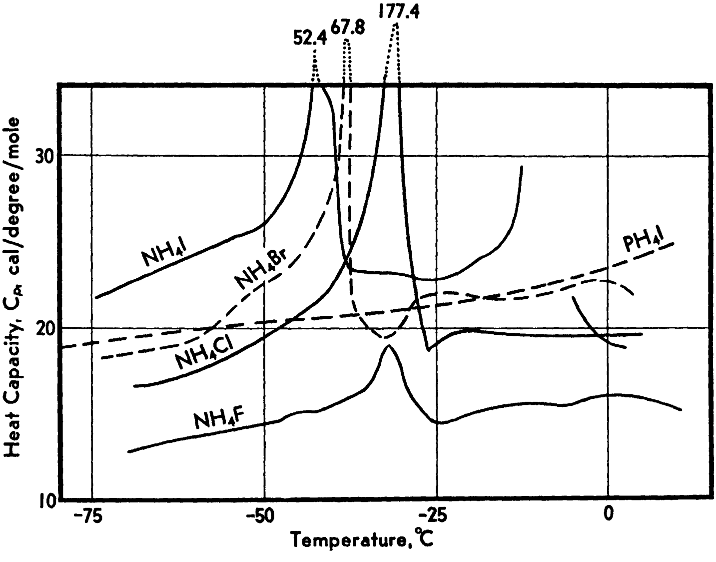


Fig. 54. The Molal Heat Capacity at Constant Pressures of Phosphonium Iodide and the Ammonium Halides.

Application of the Clapeyron equation, $dp/dt = \Delta H/T\Delta V$, is not possible if $\Delta H = \Delta V = 0$ and does not explain the facts in any event. If we consider $\Delta F(p, T) = 0$ for the transition in a finite region, Δp and ΔT near the lambda-point, then, on expanding in series, we obtain, since $\Delta F(p, T) = 0$ and $\Delta F(p + \Delta p, T + \Delta T) = 0$,

$$\left(\frac{\partial \Delta F}{\partial p}\right)_T \Delta p + \left(\frac{\partial \Delta F}{\partial T}\right)_p \Delta T + \left(\frac{\partial^2 \Delta F}{\partial p^2}\right)_T \Delta p^2 + \frac{\partial^2 \Delta F}{\partial p \partial T} \Delta p \Delta T + \left(\frac{\partial^2 \Delta F}{\partial T^2}\right)_p \Delta T^2 + \cdots = 0$$

or, replacing the derivatives by their equivalent,

$$\Delta V \Delta p - \frac{\Delta H}{T} \Delta T + \left(\frac{\partial \Delta V}{\partial p}\right)_T \Delta p^2 + \left(\frac{\partial \Delta V}{\partial T}\right)_p \Delta p \Delta T - \frac{\Delta C_p}{T} \Delta T^2 + \cdots = 0.$$

If Δp and ΔT are taken infinitesimally small, and if the coefficients of their powers are not small or zero, we obtain the Clapeyron equation $\Delta V \Delta p - (\Delta H/T)\Delta T = 0$. But if Δp and ΔT are very small but finite, and if in addition ΔV and ΔH are small, then the "second-order" terms may be comparable in value to the first-order ones. If we assume that the third- and higher-order terms can be neglected, then we have a quadratic equation in Δp and ΔT whose graph will be a strongly curved ellipse or hyperbola with vertex near the lambda-point, according to the sign of its discriminant. At a given pressure there will be two temperatures at which one or the other form will exist. That is, if the substance is cooled at a fixed pressure, it will change from one form to the other;

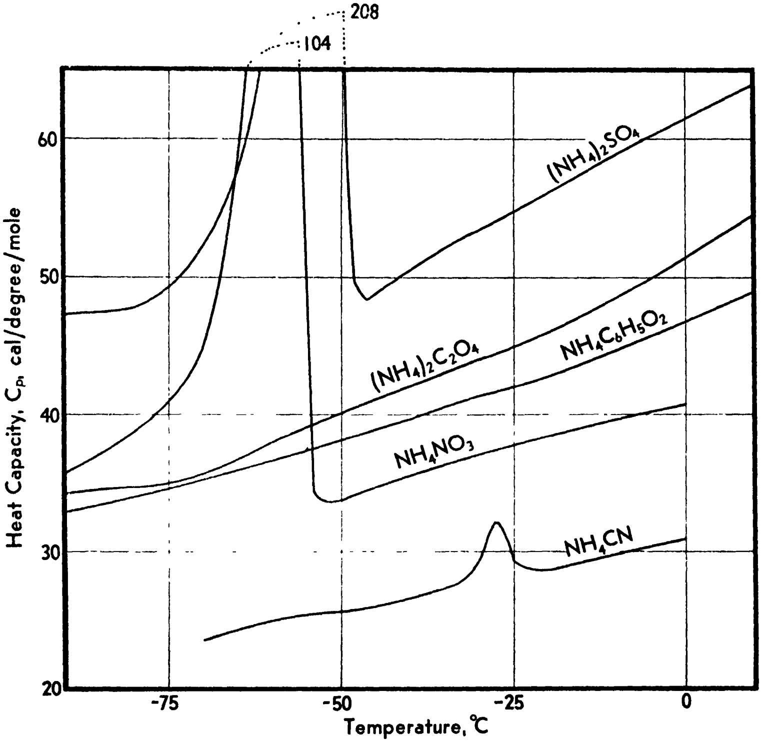


Fig. 55. The Molal Heat Capacity at Constant Pressure of Some Ammonium Salts

and on further cooling it will reach a temperature at which it will change from the second back to the first form. This is shown by the line AB in Fig. 56. The Clapeyron equation alone would permit only a single temperature for an equilibrium state at a given pressure (univariant system). [See Epstein, *Textbook of Thermodynamics,* p. 132.]

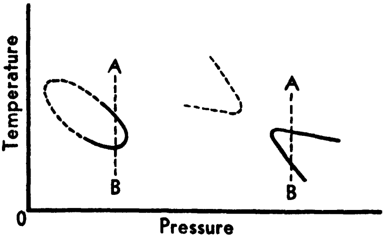


Fig. 56. Special Cases of Second-order Equilibria.

Many attempts have been made to give an explanation of the second-order transitions in terms of energy states of the molecules or ions in the crystals. The simplest of these assumes that a restricted rotation (oscillation of an NH_4^+ about its axis) becomes free on picking up the additional energy resulting from the temperature increase. According to the equations of quantum statistics for non-interacting molecules, one would, for such a situation, find a hump in the C_p, T curve. The matter is not quite so simple as assumed, however, since the motion of any one NH_4^+ will be appreciably affected by the vibrational or rotational states of its neighbors, and the partition functions to be used will contain the energy in a complicated way. The simple theory is probably correct in its main, general features, however; the transitions of the second order doubtless correspond to changes from a well-ordered arrangement of the molecular orientations to a more chaotic one, or vice versa. For a more detailed discussion of the various theories and their application to experimental results, the reader is referred to the review article by Eucken.

CHAPTER 8

Oxygen, Sulfur, Selenium, Tellurium, and Their Compounds with Hydrogen

Oxygen

Preparation

Oxygen may be prepared by heating a number of oxides, HgO, PbO_2, BaO_2, some oxyacids, $KClO_3$, $K_2Cr_2O_7$, and, most conveniently for very pure oxygen, dried $KMnO_4$. A very pure product may also be obtained by electrolyzing sodium hydroxide solutions. Oxygen is an important article of commerce, the gas being compressed in steel cylinders at 3000 lb gauge or less. For this purpose it is obtained by the fractional distillation of liquid air at pressures varying from one to five or ten atmospheres.

Physical properties

The oxygen molecule is diatomic, O_2, at ordinary pressures, but at high pressures there is evidence for believing that O_4 molecules are also present in small concentrations. The evidence consists in the fact that at moderate or low pressures gaseous oxygen is paramagnetic, the susceptibility per mole at low pressures being given quite accurately as a function of the temperature for low magnetic fields by

$$\chi_m = \frac{1.011}{T} \text{ e.m.u.}$$

[Bauer and Piccard, *J. de Phys.*, **1**, 917 (1920)], and in accordance with the statistical interpretation of Curie's law, $\chi_m = \text{constant}/T$, the gas molecules O_2 have associated with them a permanent magnetic moment. The susceptibility of liquid oxygen and the gas at high pressures does not obey Curie's law.

In terms of the elementary magnetic moment μ_0 (Bohr Magneton), the quantum numbers J (total electronic angular momentum), S (total electron spin momentum), and L (total orbital momentum), and Avogadro's number, N, the molal susceptibility is given theoretically by

$$\chi_m = \frac{\mu_0^2 N^2 J(J+1) g^2}{3RT}$$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

If J, S, and L are known from spectroscopic data, then χ_m can be calculated. μ for the spin moment alone is $\mu = 2\sqrt{S(S+1)}he/4\pi mc$; for the orbital contribution alone, $\mu = \sqrt{L(L+1)}he/4\pi mc$, e being the charge and m the mass of the electron. In some cases, for example the monatomic vapors of silver, hydrogen, and the alkali metals [L. C. Lewis, *Z. Physik*, **69,** 786 (1931)], the values of J, S, and L are known, and the calculated values of μ and χ_m are in agreement with experiment. If the theory is applied to the oxygen molecule, under the assumptions that $L = 0$ (orbital magnetic moments cancel) and that two electron spins are parallel so that $J = S = 1 = 2 \times \frac{1}{2}$, then, since $\mu_0 N = 5585$ erg/gauss/mole, and $g = 2$,

$$\chi_m = \frac{(5585)^2 \times 2 \times 2^2}{3 \times 8.37 \times 10^7 T} = \frac{0.994}{T}$$

which is in excellent agreement with the experimental value given above. Consequently, the diatomic oxygen molecule contains two unpaired electrons in spite of the fact that the molecule has an even number of electrons all together. The oxygen-oxygen bond may not be regarded, therefore, as simply a double bond, in which all electrons would be paired, but is more complex and probably involves three-electron bonds [Pauling, *The Nature of the Chemical Bond*, 2nd ed., p. 272].

The magnetic susceptibility of liquid oxygen is given by

$$\chi_m = \frac{7.309 \times 10^{-2}}{T^{1/2}};$$

that is, Curie's law, $\chi_m = \text{constant}/T$, is not obeyed, and this fact is interpreted to mean that liquid oxygen contains diamagnetic O_4 molecules in equilibrium with paramagnetic O_2 molecules [G. N. Lewis, *J. Am. Chem. Soc.*, **46,** 2027 (1924)]. Liquid solutions of oxygen in nitrogen also give a lower molal susceptibility for the oxygen than is found for the gas; but as the solutions are made increasingly dilute in oxygen, the limiting susceptibility approaches that of gas. Additional evidence for the existence of O_4 molecules is provided by the absorption spectrum of oxygen at very high pressures [Finkelnburg and Steiner, *Z. Physik.*, **79,** 69 (1932); Salow and Steiner, *ibid.*, **99,** 137 (1936)]. The heat of formation of O_4 from O_2 has been estimated to be $\Delta H_{291} = -130$ cal.

Associated with the two parallel electron spins in the oxygen molecule is an angular momentum of $\sqrt{S(S+1)}\ h/2\pi$. This resultant electron-spin momentum assumes the following positions with respect to the angular momentum of the rotating molecule: approximately parallel, anti-parallel, or perpendicular. The three states corresponding to these three orientations are known as F_1, F_2, and F_3, and they differ but little in energy. Each of the O^{16} nuclei has an even number of fundamental particles; consequently, the total wave function for the oxygen molecule must be symmetric with respect to interchange of the nuclei. The O^{16} nucleus has no angular momentum (zero nuclear spin); hence, the spin wave function is symmetric. The ground electronic state is antisymmetric for an inversion of the nuclei; therefore, in order to make the total function symmetric, the rotational states must be antisymmetric. Only rotational states with K odd fulfill this requirement, and only these are observed.

If K is the quantum number for molecular rotation, J the resultant quantum number (quantum mechanical vector sum of K and S), and v the vibration quantum number, the rotational energy states for the three electronic states are given by $\epsilon_{rot.}/hc = (1.438 - 0.01596v)K(K + 1) - 4.86 \times 10^{-6}K^2(K + 1)^2 + F_i$, where, according to theory combined with experiment [Schlapp, *Phys. Rev.*, **51,** 342 (1936)],

$$K = 1, 3, 5, 7 \ldots$$

$$F_1 = (2K + 3) - \lambda - [(2K + 3)^2B^2 + \lambda^2 - 2\lambda B]^{1/2} + \mu(K + 1), \qquad J = K + 1$$

$$F_2 = 0, \qquad J = K$$

$$F_3 = -(2K + 1)B - \lambda + [(2K - 1)^2B^2 + \lambda^2 - 2\lambda B]^{1/2} - \mu K, \qquad J = K - 1$$

$$B = 1.438 \text{ cm}^{-1} \qquad \lambda = 1.985 \text{ cm}^{-1} \qquad \mu = -.008 \text{ cm}^{-1}$$

Accordingly, the three spin orientation states for the lowest rotation state ($K = 1$) would differ at most by 1.4 cm^{-1}, that is, about 4 cal/mole. It is found experimentally that the F_1 and F_3 states are very close (within 2 cm^{-1}) to the F_2 state for all values of K. It follows from this that for most thermodynamic calculations, except at very low temperatures, this energy difference may be neglected. The quantum weights, $2J + 1$, will be, at the higher temperatures, the determining factor in the distribution of molecules among the F_1, F_2, and F_3 states. In Fig. 57 is plotted the electronic plus the rotational heat capacity of a hypothetical non-condensable gas having the same energy states as oxygen; the two maxima correspond to the thermal excitation from the F_3 to the F_1 and F_2 states, respectively. At 90°K, the percentages of molecules in the F_1, F_2, and F_3 states are 42.3. 32.1. and 25.6%, respectively. The electronic state

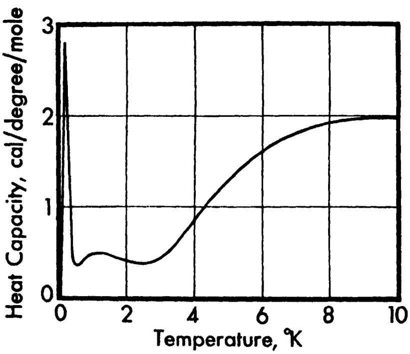


Fig. 57. The Electronic plus Rotational Heat Capacity at Low Temperatures for a Hypothetical Non-condensable Gas Having the Same Energy States as Oxygen.

of the oxygen molecule is designated by spectroscopists by the symbol $^3\Sigma_g^-$, the Σ referring to the fact that the resultant electronic orbital momentum is zero, the superscript on the left indicating the multiplicity $2S + 1 = 2(\frac{1}{2} + \frac{1}{2}) + 1 = 3$ of the electronic state, and the symbols on the right giving the symmetry properties of the wave function. In the calculation of entropies and related quantities by statistical mechanical methods, the additive term $R \log_e 3$ must be included to take account of the degeneracy of the molecular ground state if the F_1, F_2, and F_3 states are not counted as sensibly different in energy. The result so obtained must, of course, be reduced by $R \log_e 2$, since only the alternate (odd) rotation levels exist as a consequence of the homonuclear nature of the O—O molecule. [See Johnston and Walker, *J. Am. Chem. Soc.*, **55,** 172 (1933); Jevons, *Report on Band Spectra of Diatomic Molecules*, Cambridge University Press, 1932, p. 123; Herzberg, *Molecular Spectra.*]

The vibration states of oxygen in cm^{-1} may be calculated over the range of measurements from the empirical formula

$$\omega = 1580.36(v + \tfrac{1}{2}) - 12.073(v + \tfrac{1}{2})^2$$

but this expression does not yield a reliable dissociation energy, since a rather large extrapolation is involved. The dissociation energy has been determined spectroscopically from a consideration of higher electronic states to be

$$O_2(g) = 2O(g), \qquad \Delta E = 117{,}200 \text{ cal}$$

and

$$O_2(g) = 2O(g), \qquad \Delta H^\circ_{291} = 118{,}000 \text{ cal}$$

the ΔE referring to the energy absorbed to dissociate the oxygen molecule at 0°K [Herzberg, *Molecular Spectra;* Bichowsky and Rossini, *Thermochemistry*].

The calculation of the dissociation of oxygen has received considerable attention; the accompanying table contains representative values [Johnston and Walker, *J. Am. Chem. Soc.*, **55,** 5075 (1933)].

From the table it will be seen that at room temperature and one atmosphere, the equilibrium partial pressure of monatomic oxygen is about 10^{-40} atm, which corresponds to a very small fraction of an atom per liter on the average. Not until the temperature reaches about 2000°K is the equilibrium partial pressure of the monatomic oxygen appreciable.

TABLE 62
THE DISSOCIATION OF OXYGEN
$[O_2(g) = 2O(g)]$

T (°K)	$\log_{10} P^2_O/P_{O_2}$ Pressures in Atmospheres
298.1	−80.770
600	−36 921
1200	−15.097
1800	− 7.770
2400	− 4.071
5000	1.712

The spectra from which the above information was derived are of three kinds, namely, the emission spectrum of oxygen from a discharge tube, the ultraviolet absorption bands in the region of 1850 Å, and the atmospheric absorption bands (here the sun is the source of continuous radiation) in the region 7700 to 5890 Å. Of these the latter has yielded the most important information about molecular oxygen. The Raman spectrum of oxygen served to confirm the analysis of the absorption bands.

It was not known until 1929 that oxygen consisted of more than one isotope. At that time Giauque and Johnston [*J. Am. Chem. Soc.*, **51,** 3528 (1929)] found from a further analysis of the atmospheric absorption bands photographed by Birge and Babcock that besides O^{16} small amounts of O^{17} (*ca.* 0.04%) and O^{18} (*ca.* 0.2%) are present in ordinary oxygen. These amounts are sufficient to give rise to the small difference between the physicists' ($O^{16} = 16.0000$) and chemists' (ordinary oxygen = 16.0000) atomic weight values. In terms of the physicists' standard, the atomic weight of ordinary oxygen would be 16.00436.

The important physical properties of oxygen are shown in Table 63; those of a thermodynamic character are due to Giauque and Johnston [*J. Am. Chem. Soc.*, **51,** 2300 (1929)], and to Cath [*Comm. Phys. Lab. Univ. Leiden*, **152d** (1918)].

TABLE 63
PHYSICAL-CHEMICAL PROPERTIES OF OXYGEN
(0°C = 273.10°K)

Boiling point	90.13°K
Melting point	54.39°K
Transition points	23.66°K 43.76°K
Liquid density	$1.248874 - 0.00481(T-68)$
Critical temp.	154.26°K
Critical pressure	49.71 atm
Interatomic distance	1.2076 Å
Heat of vap. at b.p.	1628.8 cal
Heat of fusion	106.3 cal
Surface tension	13.2 dynes/cm at b.p.
Heats of transition	22.42 cal 177.6 "
Dielectric constant	1.491 (at b.p.)
Magnetic suscept. of liquid O_2	$\chi = 2284 \times 10^{-6}/T^{1/2}$, per gram
Standard entropy, S°_{298}	49.03 cal/deg

Vapor pressure equation (Cath):

$$\text{Log}_{10} P_{\text{atm}} = -\frac{419.31}{T} + 5.2365 - 0.00648T$$

Inasmuch as the temperatures at the corresponding vapor pressures of pure liquid oxygen are used as fixed or standard points (on the international scale) in thermometry, the accepted vapor pressure equation is given. For this purpose pure oxygen is usually prepared by heating pure, dry potassium permanganate, $KMnO_4$.

The international temperature scale between the normal boiling points of sulfur and oxygen was established by means of a gas thermometer whose readings were corrected for gas imperfections. On the centigrade scale, the following fixed points were determined and adopted as definitive points: b.p. of sulfur, 444.60°; b.p. water, 100.000°; b.p. of oxygen, −182.97°; and f.p. of water under one atmosphere pressure, 0.000°. These temperatures serve to fix four constants in an empirical equation relating the centigrade temperature, t, to the resistance, R, of pure strain-free platinum wires fulfilling certain conditions. The equation is [see, *e.g.*, Hoge and Brickwedde, *J. Res. Nat'l Bur. Stds.*, **22,** 351 (1939)

$$t = \frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \qquad 0^\circ \leqslant t \leqslant 660^\circ$$

$$t = \frac{R_t - R_0}{\alpha R_0} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} + \beta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)^3$$

$$-182.97^\circ \leqslant t \leqslant 0^\circ$$

$$\alpha = \frac{R_{100} - R_0}{100 R_0}$$

$$\alpha \text{ must be } > 0.003900$$

$$\delta \text{ must be } < 1.50$$

$$\frac{R_{-183}}{R_0} \text{ must be } < 0.250$$

This equation then defines the international centigrade temperature scale; it agrees to within a few hundredths of a degree with the absolute thermodynamic scale T if we put $T_{\text{int}} = T_0 + \text{t}$, where $T_0 = 273.16°\text{K}$.

The value 90.13°K for the b.p. of oxygen given in the table differs from 273.16 − 182.97 = 90.19°K because T_0 was assumed to be 273.10°K instead of the more recently reported value of 273.16°K.

The heat capacity of liquid oxygen decreases with increase in temperature, and this fact is considered as further evidence for the existence of O_4 molecules; as the liquid is heated up, the concentration of O_4 molecules decreases and less and less energy is required for their dissociation into O_2.

The atmosphere

Oxygen in the atmosphere plays an all-important role in life processes. It is, for example, absorbed reversibly by the hemoglobin in the blood in the alveoli of the lungs at a partial pressure of 95–100 mm. The absorption is reversible, and the arterial blood gives up the oxygen to the tissues in passing through the capillaries, where the blood is exposed to the low partial pressure of oxygen of 35 mm. In the tissues the eventual combination of the oxygen takes place in the complicated processes of cellular oxidation which provide the energy for living.

Other constituents of air play roles of importance equal to that of oxygen. Thus nitrogen, through the agency of legumes and by artificial means, is converted by natural and artificial processes into compounds that are convertible by plants and animals into proteins and other nitrogenous substances. In addition, nitrogen acts as a diluent in air.

Another important constituent of air is carbon dioxide, which, in the presence of water and under the photochemical action of sunlight, is converted into carbohydrates in the leaves of plants. The water vapor in air prevents, by its presence, the desiccation of many varieties of plants and even animals. Present in air are the noble gases helium, neon, argon, krypton, and xenon; and, although these do not seem to be necessary in life processes, their properties have proved to be very significant to the scientist in unraveling the nature of atomic structure and chemical binding. Some of them have proved useful in industry (helium for lighter-than-air craft and for the prevention of "the bends" in divers, and neon for illuminated signs) and science (helium for obtaining very low temperatures and in the production of artificial α particles in transmutation experiments; the others for a variety of purposes).

The composition of air varies slightly with altitude, weather conditions, and geographical position. The moisture content is subject to the greatest variation; its percentage may have values from nearly zero to that corresponding to the equilibrium vapor pressure of water at the temperature of the air. Carbon dioxide is also subject to some variation in amount, especially in regions where factories are operating or people are assembled. Dry air has the following composition at sea level and in open country.

TABLE 64

COMPOSITION OF DRY AIR IN VOLUME PER CENT

Oxygen	20.95	Neon	0.0018
Nitrogen	78.09	Argon	93
Carbon Dioxide	0.03	Krypton	.0001
	(0 025 to .035)	Xenon	.000008
Helium	.00052	Hydrogen	.00005

Neon, if it could be recovered from air at only moderate cost, would prove a very welcome substitute for the somewhat dangerous hydrogen in the production of low temperatures, its boiling point being 27.1°K, which is not greatly above that of hydrogen, namely, 20.4°K. The higher liquid density of neon (Ne 1.2, H_2 0.0709) is conducive to ease in handling; furthermore, the heat of vaporization of a liter of liquid neon is nearly four times that of the same volume of liquid hydrogen.

Also present in air are small amounts of nitric oxide, carbon monoxide, and methane.

The chemical properties of oxygen

Oxygen is soluble to a small extent in water, the distribution ratio between water and the gas phase being

$$R = \frac{\text{Concentration in water}}{\text{Concentration in gas phase}} = 0.03080$$

at 25° and 0.03630 at 15°; the value of R is independent of the units used to express the concentrations. Oxygen at 760 mm pressure is soluble in benzol to the extent of 1.5 to 2 millimoles per liter of solution. It is slightly soluble in alcohol (coefficient = 0.2337 at 0°; that is, 0.2337 cc O_2 at N.T.P. will dissolve in one cc of solvent if the pressure is 1 atm) and in ether (coefficient = 0.4235 at ordinary (?) temperatures). It is absorbed by platinum black to the extent of 4.96 cc (N.T.P.) per 4.269 g of Pt black at 25°. Charcoal is also a good adsorbent for oxygen, the amount adsorbed depending on the temperature, pressure, and the nature of the charcoal. For example, one gram (2.5 cc) of activated charcoal will adsorb 10 cc of O_2 when the pressure is 760 mm and the temperature 25°; at the same pressure but at liquid air temperatures, the amount adsorbed is 20 times greater [Braunauer and Emmett, *J. Am. Chem. Soc.*, **59**, 2682 (1937)]. Charcoal, freshly degassed at 500° and placed in a vacuum system of moderate volume in which the pressure of air is about 1 mm, will, when cooled with liquid air, adsorb the air until the pressure reaches 10^{-5} mm or less, and hence serves as an excellent means for attaining a moderately high vacuum. The oxygen adsorbed by charcoal is not completely recoverable as such, some of it uniting with the carbon to form a solid oxide; this oxide, on heating, is decomposed into carbon monoxide and dioxide.

Oxygen reacts directly with most of the elements and many compounds at rates that vary over a large range and that depend on the conditions of mixing. With hydrogen at room temperatures, the reaction is well known to be extremely slow, if it takes place at all, unless the mixture is ignited or a catalyst (Pt black or finely divided Os) is introduced. The alkali metals react at moderate rates at room temperatures and more rapidly at higher temperatures to form oxides M_2O, peroxides M_2O_2, and superoxides MO_2 (best prepared by bubbling oxygen through a liquid ammonia solution of K, Rb, or Cs [Kraus and Whyte, *J. Am. Chem. Soc.*, **48**, 1789 (1926)]). The alkaline earth metals, as well as some others (Zn and Re), react to form peroxides as well as the oxides. With the exception of gold and platinum, all of the metals combine more or less readily with oxygen, the rate of reaction being usually slow at room temperatures.

A number of reducing agents in aqueous solution absorb oxygen. Thus alkaline pyrogallol, Cr^{++}, Ti^{+++}, V^{++}, V^{+++}, Fe^{++}, $SO_3^{=}$, and many others are oxidized directly by oxygen. In at least one case, Ti^{+++}, peroxide is an intermediate step in the oxidation, as is shown by the fact that, on shaking a solution of $TiCl_3$ with oxygen, completion of the reaction is accompanied by the sudden appearance of the orange color of peroxytitanic acid. Often the rate of absorption of oxygen by reducing solutions is greater the more alkaline the solution.

The whole subject of the action of oxygen on reducing substances is one of considerable interest, and the chemistry of these reactions is fundamental to innumerable processes. The mechanisms of the reactions are only beginning to be properly studied and understood.

The term *oxidation* was derived from the word *oxygen*. It should be made clear that the term is not restricted to the action of oxygen, since in the general sense now used, oxidation in inorganic chemistry often implies that the substance oxidized has lost electrons. These are gained by the oxidizing agent, whether it be oxygen or some other substance, for example, chlorine, Fe^{+++}, MnO_4^-, or sulfur. But the difficulty arises that some so-called oxidation reactions cannot be said to result in the loss and gain of electrons. Thus, in the reactions $C + O_2 = CO_2$, $Si + 2Cl_2 = SiCl_4$, and $SO_3^= + \frac{1}{2}O_2 = SO_4^=$, the electrons are believed to be shared by C and O, Si and Cl, and S and O. Thus, while the general notion of oxidation is a helpful one, care should be exercised in taking too naïve a point of view of the matter. It may be said that for some reactions, especially simple ionic ones, the notion of loss and gain of electrons is a proper one; but it certainly is not true in general.

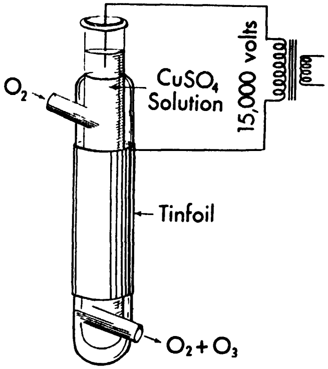


Fig. 58. An Ozone Generator.

Ozone

Preparation

Ozone is formed by the action of ultraviolet light of 1850 Å wave length or shorter on oxygen. This reaction takes place in the outer atmosphere; and since ozone is a better absorber of ultraviolet radiation than is oxygen, the earth is protected from much of the short wave length radiation given off by the sun.

Ozone is usually prepared by passing an electric discharge through oxygen at ordinary pressures. The apparatus ordinarily used consists of a double-walled glass tube with metal foil wrapped about the outside wall and with the inner tube filled with an electrolyte, for example, copper sulfate solution. The terminals of a 20,000–30,000 volt transformer are connected to the metal foil and the electrolyte, respectively, and oxygen is passed through the space between the outer and inner tube. The yield is only a few per cent and depends on a number of factors, including the source of the oxygen [Warburg, *Ann. Physik*, **9,** 781 (1900); Goldstein, *Ber.*, **36,** 3042 (1903)]. A typical ozone generator is shown diagrammatically in Fig. 58. Details of the preparation of pure ozone by fractionation have been worked out by Karrer and Wulf [*J. Am. Chem. Soc.*, **44,** 2391 (1922)].

A second method of preparation consists in the electrolysis of sulfuric acid solutions with a high current density [Fischer and Massenez, *Z. anorg. Chem.*, **52,** 202, 229 (1907); Fischer and Bendixsohn, *Z. anorg. Chem.*, **61,** 13, 183 (1909); Griffith and Shutt, *J. Chem. Soc.*, **119,** 1948 (1921)]. With a well-cooled cell containing sulfuric acid of density 1.085 g/cm³ and using current densities from 47 to 63 amp/cm², Fischer and Massenez were able to obtain an oxygen-ozone mixture containing from 18 to 25% by weight of ozone. To facilitate cooling of the anode, it is usually constructed of thin platinum tubing through which a stream of water is passed. The yield of ozone is strongly dependent on the concentration of sulfuric acid, and experiment shows that the best results are obtained when the density of the acid is 1.085 g/cm³.

A number of reactions have been reported in which ozone is said to form. In a number of these the results are subject to the criticism that the test for ozone was not unique. For example, it is generally believed that fluorine reacts with water to give ozone, but the oxidizing action of the resulting gaseous reaction products may be due to oxygen fluoride, OF_2, and not to ozone.

Physical properties

Although the absorption spectrum of ozone in the infrared has been investigated, there is not universal agreement as to its interpretation. One of the difficulties involved is that of purity; the technique of preparation and measurement is such that small amounts of oxidizable substances are often in contact with the reactive ozone, and this contact might lead to the formation of volatile, light-absorbing compounds.

An assignment of the measured bands which gives reasonable values for the force constants has been made by Sutherland and Penney [*Proc. Roy. Soc.*, **A156,** 678 (1936)].

ω_1	1037 cm^{-1}
ω_2	710 cm^{-1}
ω_3	1740 cm^{-1}

The angle estimated from these constants is about 127°. The structure of ozone has been determined recently by electron diffraction [R. A. Spurr and W. Shand, *J. Am. Chem. Soc.*, **65,** 179 (1943)]. The molecule is bent with the O—O—O $\angle = 127 \pm 5^\circ$ and the O—O distance $1.26 \pm .02$ Å. This structure is in accord with the fact that the shape of the absorption bands shows that the molecule is neither linear nor a symmetric top. The molar entropy at 298.1°K calculated from the data given above is 56.81 cal/deg. Table 65 gives values of the equilibrium pressures of ozone and oxygen calculated with the 1941 physical constants of Birge [*Rev. Mod. Phys.*, **13,** 235 (1941)]. The $^1\Delta$ state of oxygen is included in

TABLE 65

EQUILIBRIUM CONSTANTS FOR THE REACTION $O_3 = \frac{3}{2}O_2$

(Pressures are expressed in atmospheres.)

T (°K)	$\log_{10} \frac{P_{O_2}{}^{3/2}}{P_{O_3}}$
298.1	28.486
500.	18.482
1000	11.122
1500	8.664
2000	7.434
2500	6.697
3000	6.207

$S^\circ_{298.1}(O_3) = 56.81$ cal/deg; $\Delta H^\circ_{298.1} = -34{,}220$ cal; $\Delta E^\circ_0 = -34{,}513$ cal.

the calculations [Spurr and Shand, *loc. cit.*]. It is clear from the equilibrium constants that even at 3000° only a small concentration of ozone is possible in oxygen. The equilibrium constants may be used to make estimates of the amount of ozone formed in a variety of reactions. Thus it can be shown that the decomposition of $KClO_4$ can lead to no detectable amount of ozone, while the action of fluorine on water could give rise to large concentrations (or pressures) of ozone. It must not be

TABLE 66

THE PHYSICAL PROPERTIES OF OZONE

Color of Gas	Color of Liquid	Boiling Point[3]	Heat of Vaporization at b.p. (cal)
Light blue	Dark blue	−111.5° ± 0.2	2547

Freezing Point	Density of Liquid	Critical Temperature
−249.6°	1.71 (−183°) 1.46 (−111°)	−5°

Vapor pressure,[1] $\log_{10} p_{mm} = -\frac{765.7}{T} + 1.75 \log_{10} T - 0.01268T + 5.783$

Vapor pressure,[2] −193° to −183°, $\log_{10} p_{mm} = -\frac{3700}{4.571T} + 1.75 \log_{10} T - \frac{.05099T}{4.571} + 5.850$

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[1] Riesenfeld and Beja, *Z. anorg. Chem.*, **132**, 179 (1923).

[2] Spangenberg, *Z. phys. Chem.*, **119**, 419 (1926).

[3] Briner and Biedermann, *Helv. Chim. Acta*, **16**, 207 (1933)

forgotten, however, that free energy values predict only the equilibrium state and do not give any indication of whether or not a reaction written down will actually take place in a reasonable time.

The more common physical properties of ozone have not been determined with great accuracy, owing to the circumstance that the substance decomposes slowly. Liquid ozone, and the gas at high pressures, can be violently explosive; explosions of the liquid are very readily set off by dust particles or bits of organic matter; great care and special precautions should be used when preparing and handling liquid ozone in open vessels. Experiments on the liquid in closed glass systems which are definitely clean and in which only pure gases free from organic vapors are used are less dangerous.

Chemical properties

Ozone is slightly soluble in water. When the ozone pressure is 760 mm, one cubic centimeter of water dissolves the following volumes (reduced to N.T.P.) of gas: 0.494 cc at 0°; 0.454 cc at 18°. Ozone decomposes more rapidly in neutral or alkaline solutions than in acid solutions. For this reason the solubilities are determined at various concentrations of H_2SO_4 and the value for pure water found by extrapolation. Henry's law is obeyed by the acid solutions [Rothmund and Burgstaller, *Nernst-Festschr.*, 391 (1912)].

A much better solvent for ozone is carbon tetrachloride. Three cc (N.T.P.) of ozone at 760 mm pressure will dissolve in 1 cc of CCl_4 at 15°. The solutions have a beautiful blue color, the color decreasing in intensity with time as a result of decomposition of the ozone; some 15 to 20 hours elapse before the color disappears entirely [Fischer and Tropsch, *Ber.*, **50**, 765 (1917)]. Ozone dissolved in CCl_4 and $CHCl_3$ is said to decompose at about the same rate that is found for the gas phase decomposition, but the mechanism may not be the same in the two cases [Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc.*, **137A,** 211 (1931)]. Glacial acetic acid also dissolves considerable ozone with the formation of blue solutions.

Gaseous ozone decomposes at a measurable rate in the temperature range 90° to 180° according to the equation

$$O_3 = \tfrac{3}{2}O_2$$

The reaction is a complex one, some of the decomposition taking place on the walls of the vessel and some in the gas phase. The latter, homogeneous part of the reaction appears to be one of second order; the second-order rate equation is $[-d(O_3)]/dt = k_2(O_3)^2$, and $k_2 = 38$ cc/mole sec at 90°. Considerable difficulty has been experienced in arriving at a satisfactory mechanism for the reaction [Wulf and Tolman, *J. Am. Chem*

Soc., **49,** 1650 (1927); Shumacher and Sprenger, *Z. phys. Chem.*, **11B,** 38 (1930); Wulf, *J. Am. Chem. Soc.*, **54,** 156 (1932); Kassel, *Kinetics of Homogeneous Gas Reactions*, p. 264] in spite of the apparent simplicity of the second-order part.

The decomposition of ozone is catalyzed by a number of gases, for example, N_2O_5, Cl_2, and Br_2. The first catalyst is of interest because N_2O_5 itself decomposes slowly with known rates to form NO_2 and O_2, and with O_3 the rapid reaction

$$2NO_2 + O_3 = N_2O_5 + O_2$$

takes place nearly quantitatively. It might be supposed that at 20° the rate of disappearance of O_3 would depend solely on the decomposition rate for N_2O_5; but as a matter of fact it is much greater, and to explain this, mechanisms involving the unknown N_2O_6 or NO_3 have been assumed but without complete success (see Kassel, *loc. cit.*). The empirical rate equation is

$$-\frac{d[O_3]}{dt} = 2k[N_2O_5]^{2/3}[O_3]^{2/3}$$

$$k = 0.0245\ (\text{cc mole}^{-1})^{1/3}/\text{sec at } 20^\circ$$
$$k = 0.135\ (\text{cc mole}^{-1})^{1/3}/\text{sec at } 35^\circ$$

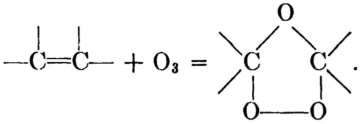
[White and Tolman, *J. Am. Chem. Soc.*, **47,** 1240 (1925); Shumacher and Sprenger, *Z. phys. Chem.*, **2B,** 266 (1929); Kassel, *loc. cit.*]. The catalysts Cl_2 and Br_2 are of interest in that the compounds Cl_2O_6 and $Br_2O_5 \cdot BrO_3$ are formed. In the case of chlorine, the rate of O_3 decomposition is measurable at 35–50°, while with bromine, the ozone decomposes slowly at first and then a few seconds later explosively at these temperatures, but the rate becomes measurable at 8° and lower. The rate at the lower temperatures with 10 mm Br_2 and 100 mm O_3 behaves in a peculiar manner, going through a maximum, a minimum, another sharp maximum, and then decreasing rapidly. Mixtures of Br_2 and O_3 at 8° or less react to form a white deposit on the walls of the vessel, the composition of which corresponds to Br_3O_8 and, if this composition is correct, may correspond to $Br_2O_5 \cdot BrO_3$, a mixture of penta and hexavalent bromine. The white solid decomposes readily at room temperatures or even lower to give bromine and oxygen [B. Lewis and Shumacher, *Z. phys. Chem.*, **6B,** 423 (1930)]. A number of solid substances act as catalysts in the decomposition of ozone; this seems natural, since the thermal decomposition of O_3 always takes place in part on the walls of the container.

Ozone is a strong oxidizing agent, the oxidation frequently resulting in the reduction of only one of the oxygen atoms to an oxide oxygen atom. This is the case, for example, in the reaction $2NO_2 + O_3 = N_2O_5 + O_2$ (rapid) mentioned above, and in the analogous reaction $NOCl + O_3 =$

NO_2Cl (rapid). Similarly, the well-known reaction with neutral iodide solutions

$$2I^- + H_2O + O_3 = I_2 + 2OH^- + O_2$$

which is used for the analysis of ozone, consumes only one atom of oxygen. The same remarks apply to H_3AsO_3 and Tl^+ solutions, both of these substances being used in the quantitative determination of ozone [A. A. Noyes, Coryell, Stitt, and Kossiakoff, *J. Am. Chem. Soc.*, **59,** 1316 (1937)]. In other reactions the whole ozone molecule combines with the reactant, this behavior being observed with organic compounds containing double bonds,



It is, of course, possible for all these oxygen atoms to combine as oxide oxygen, as would happen, for example, if a mixture of ozone and hydrogen were caused to explode.

Qualitative tests for ozone often do not distinguish it from other oxidizing agents. A satisfactory test is said to consist in the use of paper soaked in an alcoholic solution of tetramethyldiaminodiphenylmethane, $(CH_3)_2N{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}N(CH_3)_2$; the moist paper shows the following color changes [Arnold and Mentzel, *Ber.*, **35,** 1324 (1902)]:

O_3	Violet
NO_2	Straw-yellow
Cl_2 or Br_2	Blue
H_2O_2	Remains colorless

The test is more sensitive if a small amount of acetic acid is present.

The powerful oxidizing action of ozone is best shown in its action on silver nitrate solutions, the Ag^+ being oxidized to Ag^{++} and Ag^{+++}, and this will precipitate out as the black AgO if the solution is neutral. The Ag^{++} remains in solution as such if the solution contains nitric acid at a concentration of 6 n or greater; the solutions are dark-colored and slowly decompose according to the reaction $4Ag^{++} + 2H_2O = 4Ag^+ + 4H^+ + O_2$. [For a detailed study of the $Ag^+ + O_3$ reaction, see A. A. Noyes, Coryell, Stitt, and Kossiakoff, *J. Am. Chem. Soc.*, **59,** 1316 (1937).] Tl^+ and Co^{++} solutions are oxidized to Tl^{+++} and Co^{+++} by ozone, but Ni^{++} does not appear to be affected. Metallic silver is discolored by ozone, the black substance formed being AgO or Ag_2O_3. Mercury is also readily attacked by ozone, the reaction and the oxide formed preventing the use of mercury manometers in measuring the pressures of gases containing ozone.

Aqueous solutions of ozone and hydrogen peroxide react to give oxygen and water. The over-all reactions are [Rothmund and Burgstaller, *Monatshefte,* **38,** 295 (1917)]

$$2O_3 = 3O_2$$
$$H_2O_2 + O_3 = H_2O + 2O_2$$

and it has been shown by Bray [*J. Am. Chem. Soc.*, **60,** 82 (1938)] that the ratio of the rates is, as a first approximation,

$$\frac{-d(O_3)/dt}{-d(H_2O_2)/dt} = \frac{1 + 5.2(O_3)}{(H_2O_2)}$$

Traube and Bray [*J. Am. Chem. Soc.*, **62,** 3357 (1940)] have found in a further study that the reactions are chain reactions and that the only mechanism consistent with all experimental results is

$$H_2O_2 + O_3 = HO + HO_2 + O_2 \qquad (1)$$
$$HO_2 + O_3 = HO + 2O_2 \qquad (2)$$
$$HO + O_3 = HO_2 + O_2 \qquad (3)$$
$$HO + H_2O_2 = HO_2 + H_2O \qquad (4)$$

Reaction (1) is the chain-initiating step. The net result of (2) and (3) is the chain decomposition of ozone. Similarly (2) and (4) constitute a chain process for the reaction between peroxide and ozone. Chloride ion, aliphatic acids (except formic acid), and alcohols are inhibitors for both reactions. The specific rate constant at 0° of the bimolecular reaction (1) was found by independent experiments with the inhibitors acetic acid and chloride ion to be 0.13 and 0.14 liters moles^{-1} min^{-1}.

Although precise values for the free energies of ozone and superoxides are not known, the following estimates are doubtless of the right order of magnitude. All free-energy values given refer to the monatomic elements at 298.1°K and one atmosphere as the substances from which the compounds are formed; ΔH_0° values refer to the formation at 0°K from the monatomic elements. There are included the data for other compounds as well, in order to render more convenient the calculation of the energy changes for a number of reactions, such as, for example, those given in the above mechanisms A and B.

	$-\Delta H_0^\circ$ (kcal)	$-\Delta F_{298}^\circ$ (kcal)		$-\Delta H_0^\circ$ (kcal)	$-\Delta F_{298}^\circ$ (kcal)
$H_2(g)$	102	95	$H_2O_2(g)$	253	230
$O_2(g)$	117	110	$H_2O_2(aq)$	—	237
$O_3(g)$	141	126	$HO(g)$	104	97
$H_2O(g)$	219	205	$HO_2(g)$	169	155
$H_2O(l)$	—	207			

Many applications of the oxidizing action of ozone have been sought and tried in the field of medicine and sanitation. In some of these at least, the action on the tissues has been harmful. The use of ozone to purify the air is of doubtful value, although the deodorizing effect appears to have some virtue.

Water

Formation

The formation of water from the elements has been much investigated. Some mixtures of hydrogen and oxygen will not, when heated or ignited, explode; thus a mixture containing 1% or less of hydrogen will not explode even when subjected to an electrical discharge. Mixtures with hydrogen at concentrations higher than 1% will ignite and explode. Equivalent quantities of H_2 and O_2 at a total pressure of 600 mm or less react at a measurable or zero rate if the temperature does not exceed about 570°; at higher temperatures, explosions occur. In these mixtures explosions will, of course, occur if the gas is ignited. The detailed mechanism of the combination of hydrogen and oxygen has not been established; the fact that surface catalysts (Pt black, Pd black, Os black) and the nature of container surfaces play an important role adds to the complexity. Small amounts of nitrogen dioxide promote explosions in equivalent mixtures, while larger amounts will inhibit them at a given temperature [Gibson and Hinshelwood, *Trans. Faraday Soc.*, **24,** 559 (1928)].

Water is formed in a great variety of reactions such as those involving the reduction of oxides by hydrogen and those in which OH^- or an oxide oxygen combines with H^+.

Physical properties

Two physical constants of water in contact with air, the melting and boiling temperatures, have defined values. The temperature of water boiling under 760.00 mm pressure is defined as 100.000°C; more precisely, the pressure under which boiling is to take place is that due to a column of mercury 760.00 mm high having a mass of 13.5951 g/cc and subject to a gravitational acceleration of 980.665 cm/sec^2. This pressure corresponds to a 760.00-mm column of pure mercury whose temperature is 0°C, and to a location where $g = 980.665$ cm/sec^2 [Burgess, *U.S. Bur. Stds. J. Res.*, **1,** 635 (1928); Beattie and Blaisdell, *Proc. Am. Acad. Arts and Sci.*, **71,** 361 (1937)]. The temperature of the steam from the boiling water is taken as 100.000° rather than that of the liquid, since the temperature of the latter may fluctuate as a result of momentary superheatings. The temperature of melting ice under an external atmospheric pressure of 760.00 mm is defined as 0.000°C; the zero of the centigrade scale is not, therefore, defined for pure water, but rather for a saturated solution of air in water. The triple point of water under its own vapor pressure of 4.579 mm is 0.0098°C. It is also common, but not desirable, to define the calorie in terms of the specific heat of water; many careful workers prefer to define the calorie as 4.1833 international joules—4.1850 absolute joules—since measurements of electrical quantities can be made with much greater accuracy than those of thermal quantities. Moreover, calorimetry makes much use of measurements of electrical energy.

In the following Table 67 are included data not only for H_2O but also for D_2O, heavy water. Heavy water can be purchased now for two or three dollars per gram, and the price will doubtless be lower in the future. The very important part played by D and D_2O in physics and chemistry cannot be overemphasized.

Ordinary water contains a small amount of heavy water, D_2O, and HDO. The percentage of deuterium is about 0.02% of the total hydro-

Table 67

THE PHYSICAL PROPERTIES OF WATER

	Melting Point (°C)	Boiling Point (°C)	Heat of Fusion (cal†)	Heat of Vaporization (cal†)	Density (g/cc)
H_2O...	0 000	100.000	1437 (0°)	10,514 (25°) 9,723 (100°)	0.999841 (0°) .999973 (4°)* .997044 (25°)
D_2O....	3.82	101.4	1501 (3.82°)	12,636 (subl. 0°)	1.1079 (25°)

	Heat of Formation (cal)	Free-Energy Formation of Liquid (cal)	Entropy S°_{298} of Gas (cal/deg)	Entropy S°_{298}, Liquid (cal/deg)	Dielectric Constant
H_2O...	68,313 (25°)	−56,685 (25°)	45.13	16.74	81.50 (17°)
D_2O....			47.38	18.08	79 (20°) $D_2/D_1 = 0.990$ (25°)

* At 3.98°C the density of pure water is 0.999973 g/cc or 1.000000 g/ml.

† All energy quanitties are for one formula weight of water, and are expressed in defined calories, 1 calorie = 4.1833 international joules.

Surface Tension, γ (dynes/cm)

Temperature (°C)	γ	Temperature (°C)	γ
−5	76.4	25	71.97
0	75.6	50	67.91
15	73.49	100	58.9

TABLE 67 (*Cont.*)

Heat Capacities of Liquid Water, H_2O (cal/deg)

t (°C)	C_p	t (°C)	C_p	t (°C)	C_p
0	18.160	40	17.962	70	18.039
10	18.050	50	18 001	80	18.069
20	18.006	60	18 017	100	18.153
30	17.991				

Heat Capacities of Ice, H_2O (cal/deg)

T (°K)	C_p	T (°K)	C_p
10	0.066	200	6.744
50	1.896	250	8 326
100	3.796	270	8.960

Heat Capacities of D_2O (solid below 276.92°K) (cal/deg)

T (°K)	C_p	T (°K)	C_p
20	0.532	250	9.842
50	1.977	270	10.54
100	4.047	280	20.15
200	8.050	295	19.78

Vapor Pressures of Solid and Liquid H_2O and D_2O in mm Hg

t (°C)	H_2O	D_2O	t (°C)	H_2O	D_2O
−90	0.000070	—	50	92.51	83.37
−30	.2859	—	70	233.7	215.9
0.0098	4.579	3.65	90	525.76	495.
25	23.756	20.63	100	760.0	722.3

Free-energy equation for $H_2(g) + \frac{1}{2}O_2(g) = H_2O(g)$:

$$\Delta F^{\circ}_{T} = -57{,}410 + 0.94T \log_e T + 0.00165T^2 - 3.7 \times 10^{-7}T^3 + 3.92T$$

gen content of ordinary water. The deuterium in ordinary water may be concentrated by electrolysis of concentrated alkaline solutions of the latter; hydrogen, H, is liberated more rapidly in the electrolysis than is deuterium [Urey and Teal, *Rev. Mod. Phys.*, **7,** 34 (1935)]. [For properties of D_2O, see Clusius, *Z. phys. Chem.*, **28B,** 167 (1935); Lewis and McDonald, *J. Am. Chem. Soc.*, **55,** 3057 (1933); Miles and Menzies, *J. Am. Chem. Soc.*, **58,** 1067 (1936); Long and Kemp, *J. Am. Chem. Soc.*, **58,** 1829 (1936).]

The behavior of water and ice under pressure has been carefully investigated by Bridgman [*Proc. Am. Acad.*, **47**, 440 (1912)]. In Fig. 59 is shown the phase diagram with the regions of existence of the various crystalline modifications of ice properly labeled. The compressibility of the water at 0° and 22°C may be seen in the table of representative values; V_0 is the volume of liquid at 1 kg/cm². The volume change attending the melting of ice, I, varies with the equilibrium temperature.

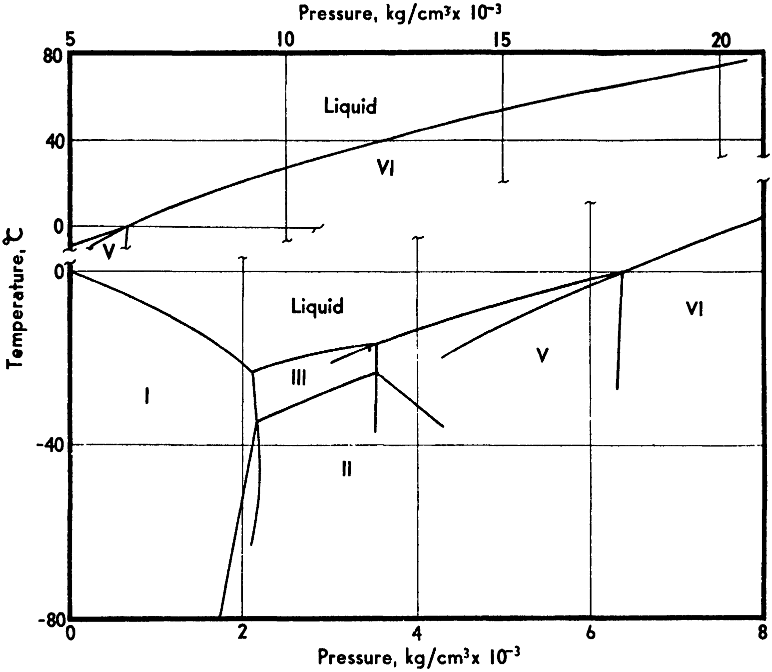


Fig. 59. The Phase Diagram for Ice.

Pressure (kg/cm²)	$\frac{\Delta V}{V_0}$ (0°C)	$\frac{\Delta V}{V_0}$ (22°C)
500	0.0224	—
1000	.0414	0.0383
2000	.0735	.0679
4000	.1195	.1137
6000	.1520	.1465
7000	.1644	.1600
11000	—	.2042

The infrared and near-infrared absorption spectrum has been investigated repeatedly, and while there is still some disagreement and uncertainty as to details of the analysis, it can safely be said that we have fairly complete information on the structure of the water molecule. The experimental results of Mecke, Badger, and others have been employed by Gordon [*J. Chem. Phys.*, **2**, 65 (1934)] and by Giauque [*e.g.*, *J. Am. Chem. Soc.*, **79**, 560 (1937)] to evaluate the thermodynamic properties of water vapor. The various energy states of the water molecule are given by empirical formulas in Table 68 [Darling and Dennison, *Phys. Rev.*, **57,** 128 (1940)].

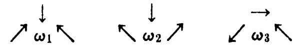
The terms in higher powers of $v + \frac{1}{2}$ are, for the vibrational states, a measure of the non-harmonic nature of the vibrations. The dependence of A, B, and C, the moments of inertia, on v_1, v_2, v_3 shows the effect of the vibrational states on the interatomic distances and bond angle. These effects obtain in all polyatomic molecules but have not been as accurately measured as those in water vapor.

The atoms in the water molecule lie, on the average, at the corners of an isosceles triangle, the symmetry axis passing through the oxygen atom and being perpendicular to the line joining the hydrogen atoms. Such a molecule has three principal moments of inertia, and a knowledge of their values permits the calculation of the interatomic distances and bond angles. It is to be noted that in any statistical calculations for the water molecule, the symmetry of the molecule must be taken into account.

TABLE 68

MOLECULAR CONSTANTS OF H_2O AND D_2O

Vibrational States



$$\frac{\epsilon}{hc} = \sum_i \omega_i(v_i + \tfrac{1}{2}) + \sum_{i>k}\sum x_{ik}(v_i + \tfrac{1}{2})(v_k + \tfrac{1}{2}) \text{ in cm}^{-1}$$

H_2O

$\omega_1 = 3825.32$ $x_{11} = -43.89$ $x_{12} = -20.02$
$\omega_2 = 1653.91$ $x_{22} = -19.5$ $x_{13} = -155.06$
$\omega_3 = 3935.59$ $x_{33} = -46.37$ $x_{23} = -19.81$
$v = 1, 2, 3 \ldots$

Moments of Inertia in gcm^2

$$A \times 10^{40} = 1.0229 + (0.0123)(v_1 + \tfrac{1}{2}) - (0.1010)(v_2 + \tfrac{1}{2}) + (0.0486)(v_3 + \tfrac{1}{2})$$
$$B \times 10^{40} = 1.9207 + (0.0398)(v_1 + \tfrac{1}{2}) - (0.0249)(v_2 + \tfrac{1}{2}) + (0.0077)(v_3 + \tfrac{1}{2})$$
$$C \times 10^{40} = 2.9436 + (0.0611)(v_1 + \tfrac{1}{2}) - (0.0385)(v_2 + \tfrac{1}{2}) + (0.0441)(v_3 + \tfrac{1}{2})$$

H—O bond, .9580 Å H—O—H angle, 104°31′

D_2O

$\omega_1 = 2758.06$ $x_{11} = -22.81$ $x_{12} = -10.56$
$\omega_2 = 1210.25$ $x_{22} = -10.44$ $x_{13} = -81.92$
$\omega_3 = 2883.79$ $x_{33} = -24.90$ $x_{23} = -10.62$

Highly accurate moments of inertia have not yet been evaluated, although the rotational spectrum has been analyzed. [Fuson, Randall, and Dennison, *Phys. Rev.* **56,** 982 (1939).] Close values are (in gcm^2):

$A \times 10^{40} = 1.790$ $B \times 10^{40} = 3.812$ $C \times 10^{40} = 5.752$

The standard entropy of water vapor, as determined experimentally from heat capacity measurements, is 0.82 cal/deg less than that calculated from spectroscopic data. The reason suggested by Pauling for this result is that the hydrogen atoms or bonds in crystal water (ice) are possessed of a limited randomness in their orientation or position at the lowest temperatures (15°K) at which heat capacity measurements were made, hence the extrapolated entropy of ice is not zero at 0°K, as would be the case if the arrangement were well ordered; the residual molal entropy of the non-well-ordered crystals is 0.806 cal/deg [Pauling, *J. Am. Chem. Soc.*, **57**, 2680 (1935)]. The results of crystal-structure investigations—which show that each oxygen atom in ice is tetrahedrally surrounded by four equivalent oxygen atoms, but that the oxygen-oxygen distance, 2.76 Å, is greater than twice the normal oxygen-hydrogen distance—had previously led Bernal and Fowler to the erroneous hypothesis that the arrangement of the water molecules in the crystal is regular at low temperatures; in reality, ice is a perfect crystal only in that the oxygen atoms are regularly arranged [Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933); see also Katzoff, *J. Chem. Phys.*, **2**, 841 (1934)]. Two of the four hydrogens nearest to an oxygen atom are "chemically bonded" with O—H = 0.99 Å, and the other two "hydrogen bonded" at 1.77 Å; the four hydrogens lie on lines joining the oxygen atom with its four nearest oxygen atom neighbors. The entropy of heavy water, D_2O, as determined from heat capacity measurements, is 0.77 less than that calculated, and the difference is given the same explanation as that advanced for H_2O [Long and Kemp, *J. Am. Chem. Soc.*, **58**, 1829 (1936)]. The difference is, within the limits of experimental error, the same for D_2O as for H_2O, and this indicates that hydrogen and deuterium atoms or bonds in ice behave in the same manner. It may be shown that the randomness in orientation or position of H or D in ice requires the addition of $R \log_e \frac{6}{4}$ (= 0.806) to the experimentally determined entropy of H_2O or D_2O.

TABLE 69
THE CALCULATED DISSOCIATION OF WATER VAPOR
$H_2O(g) = H_2(g) + \frac{1}{2}O_2(g)$
(Pressures in atmospheres. α = Degree of dissociation. $\Delta E_0^\circ = 57{,}120$ cal.)

T (°K)	$\log_{10} \dfrac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}$	α
1300	−7.070	2.44×10^{-5}
1500	−5.725	1.92×10^{-4}
1800	−4.260	0.00182
2000	−3.525	.00563
2400	−2.417	.0308
2800	−1.614	.106
3000	−1.290	.174

From the heat of formation of water and spectroscopic data

$$\log_{10} \frac{P_{H_2}P_{O_2}^{1/2}}{P_{H_2O}}$$

has been calculated for a number of temperatures. Representative values are shown in Table 69 [see *e.g.*, Gordon, *J. Chem. Phys.*, **2**, 549 (1934)].

Chemical properties

The high dielectric constant, 81, of liquid water indicates a highly polar molecule and the existence of polymers. The Raman spectrum of water contains a number of lines and is interpreted provisionally as resulting from water molecules coordinated with two or more other water molecules—by hydrogen bonds or bridges; this interpretation does not imply that liquid water consists of well-defined polymers, however [Cross and Leighton, *J. Am. Chem. Soc.*, **59**, 1134 (1937)]. The hydrogen bond is pictured as consisting of a proton (and possibly its attendant electron) shared by two oxygen atoms; the positively charged proton attracts two negatively charged oxygens and thus holds the H_2O molecules together. In ice each H_2O is surrounded at tetrahedron corners by four other H_2O, but that this configuration obtains in liquid water does not, of course, follow.

One consequence of the highly polar character of water is its action as a strongly ionizing solvent. It is capable also of combining with many solutes (SO_2, NH_3, P_2O_5, Na_2O, to mention only a few) to form acids and bases. Many reactions may be said to be catalyzed by water, and the intermediates responsible for the catalysis are doubtless often some ion or ions that owe their existence to the presence of water. It does not follow of course that all reactions are between ions. Some reactions are promoted by water by virtue of its wetting action; thus, gold covered by cyanide solutions is oxidized by atmospheric oxygen to $Au(CN)_2^-$, but without the solvent the contact and diffusion of a solid cyanide would not be sufficient to result in the formation of much $MAu(CN)_2$. The role of water in life processes as a carrier of solutes and as a participant itself is an important one.

Water combines with many substances to form hydrates. In such cases the water molecules may often occupy coordination positions in the same manner as does ammonia. In some hydrates the water molecules fill up "holes" in the crystal and are not regarded formally as occupying coordination positions.

Water acts as both an oxidizing and a reducing agent. Thus it oxidizes the alkali and alkaline earth metals, iron, aluminum, Ti^{++}, and other strong reducing agents with the evolution of hydrogen. The hydrogen of the water may be regarded as the oxidizing agent. Water will reduce fluorine, chlorine, permanganate, Ag_2O_3, and other strong oxidizing agents, with the evolution of oxygen, the oxide oxygen of water acting as the reducing constituent.

The chemical reactions taking place in heavy water differ somewhat but not greatly from those in ordinary water. Thus, degrees of ionization of weak electrolytes are smaller in heavy water than in ordinary water. Bromine hydrolyzes less in D_2O. Some reaction rates are greater in D_2O (for example, $BrO_3^- + I^-$) than in H_2O [Abel and Fabian, *Chem. Abstracts*, **31**, 2073 (1937)]. The dissociation constant of heavy water is less than that of ordinary water. At 25° the constants for both are

$$H_2O = H^+ + OH^- \qquad (H^+)(OH^-) = 10^{-14}$$
$$D_2O = D^+ + OD^- \qquad (D^+)(OD^-) = 1.6 \times 10^{-15}$$

[Abel, Bratu, and Redlich, *Z. phys. Chem.*, **173A,** 353 (1935)]. The ionization constant of heavy acetic acid CH_3COOD in $D_2O(l)$ is less than that of CH_3COOH in $H_2O(l)$, thus calling the acids DAc and HAc [G. N. Lewis and Schutz, *J. Am. Chem. Soc.*, **56,** 1002 (1934)],

$$DAc = D^+ + Ac^- \qquad \frac{(D^+)(Ac^-)}{(DAc)} = 0.59 \times 10^{-5} \text{ at } 25°$$
$$HAc = H^+ + Ac^- \qquad \frac{(H^+)(Ac^-)}{(HAc)} = 1.84 \times 10^{-5} \text{ at } 25°$$

The differences are seen to be measurable and of moderate magnitude. The cause of the differences lies for the most part in the mass differences, since the bonds formed by D and H are probably of nearly equal strength.

Sulfur, Selenium, and Tellurium

Preparation

Sulfur occurs in nature in the elementary form, and the product so obtained can be highly purified by simple distillation. It may be found in the form of large, pure or nearly pure crystals or intimately admixed with silica and other siliceous materials. In either case the sulfur is easily soluble in carbon bisulfide and hence is present as the rhombic modification and not as the insoluble or amorphous form. Sulfur is commonly sold as "brimstone," formed by allowing molten sulfur to solidify, and as the very finely divided flowers of sulfur, which results when vapors of sulfur are allowed to condense rapidly. Neither of these products is a single modification; both contain the insoluble or amorphous sulfur together with the soluble form.

Selenium is found ordinarily in the form of selenides; these as well as the impure selenium of commerce can be oxidized readily to selenites with 6 n HNO_3, and the selenites can then be reduced to selenium with H_2SO_3, hydrazine, iodide, and other reducing agents. The principal impurity will be Te, but if the reduction is carried out in 10–12 n HCl, Te will not be precipitated. The selenites can also be converted to SeO_2, and this may be purified by sublimation before it is reduced.

Tellurium occurs in nature in the form of tellurides, for example as gold telluride AuTe. These can be oxidized readily with nitric acid or oxygen to form the dioxide, TeO_2. The dioxide frequently contains copper as an impurity. Elementary tellurium can be precipitated from hot, 2 n HCl solutions of TeO_2 by reduction with H_2SO_3. The preparation of highly purified tellurium requires more labor than is the case with sulfur and selenium, since the impurities selenium and especially copper are not readily separated. The separation from copper is attained by converting the elementary tellurium to $2TeO_2 \cdot HNO_3$ by the action of strong (d. 1.250) nitric acid at 70°. The basic nitrate can be recrystallized readily from the nitric acid solution by evaporating on a steam bath at 80°; it is then free from copper. Any selenium is removed by treating a warm 10 n HCl solution of TeO_2 (formed by igniting the basic nitrate strongly) with SO_2 [see *e.g.*, Schuhmann, *J. Am. Chem. Soc.*, **47,** 356 (1925)]. It is noteworthy that reduction of tetravalent tellurium by sulfurous acid takes place completely in hot 2 n hydrochloric acid; but if the acid is concentrated, 10 n, little if any reduction occurs.

Properties of solid and liquid S, Se, and Te

A number of crystalline forms of sulfur have been identified by their external appearance and optical properties. The forms reported and their suggested order of stability [Korinth, *Z. anorg. Chem.*, **174,** 57 (1928)] are:

$$S_\theta \text{ (tetrahedral)} \rightarrow S_\delta \text{ (monoclinic)} \rightarrow S_\eta \text{ (monoclinic)} \rightarrow S_\rho \text{ (monoclinic)} \rightarrow$$

$$S_\gamma \text{ (monoclinic)} \rightarrow S_\beta \text{ (the usual monoclinic S)} \overset{95.5^\circ}{\rightleftharpoons} S_\alpha \text{ (rhombic sulfur)}$$

Not classified are S_ρ (or S_ϵ) (trigonal) and S_ξ (triclinic).

Most of these forms have been identified under the microscope after crystallization under special conditions (for example, for S_γ, sulfur is heated to 150°C, cooled to 90°, and crystallization initiated by rubbing the beaker; for S_δ, sulfur in $(NH_4)_2S$ solution is cooled to 5°; for S_θ, sulfur is crystallized from CS_2 thickened with balsam). The more important forms are S_ρ, S_β, and S_α, and they are discussed more fully below.

The rhombic crystalline form of sulfur is thermodynamically stable at room temperature. It is a yellow solid with a density of 2.07 g/cm³. An X-ray investigation has shown the crystals to be made up of S_8 molecules, 16 in a unit cell, arranged approximately in layers perpendicular to the *c*-axis. The molecules are puckered rings with angles of 105° and an S-S distance of 2.12 Å [Warren and Burwell, *J. Chem. Phys.* **3,** 6 (1935)]. When a solution of sulfur in carbon bisulfide is allowed to evaporate, crystals of rhombic sulfur are deposited. If rhombic sulfur is heated to 100° or a little less and maintained at that temperature for several hours, the crystals become opaque and consist of aggregates of the monoclinic form; the transition temperature is 95.5°. Monoclinic sulfur is also formed when molten sulfur is allowed to crystallize slowly, beautiful needle-shaped crystals being formed if the liquid, soon after a crust or skin begins to form, is poured into another vessel. The density of monoclinic sulfur is 1.96 g/cm³ and the color is pale yellow. The atomic heat of transition is 95 cal [Bronsted, *Z. phys*

Chem., **55**, 371 (1906)], that is

$$\text{S (rhombic)} = \text{S (monoclinic)}, \Delta H^\circ_{368.6} = 95 \text{ cal.}$$

The atomic heat capacities of rhombic and monoclinic sulfur can be represented over a limited range (250 to 368.5°K) by the following empirical formulas [calculated from the experimental data of Eastman and McGavock, *J. Am. Chem. Soc.*, **59**, 145 (1937)]:

$$C_p \text{ (rhombic)} = 3.493 + 0.00636T$$
$$C_p \text{ (monoclinic)} = 3.556 + 0.00698T$$

These formulas, taken together with $\Delta H^\circ_{368.5}$ and the fact that $\Delta F^\circ_{368.5} = 0$, permit the calculation of ΔF°_T. If monoclinic sulfur is allowed to stand for a few days at room temperature, it changes into rhombic sulfur, although the monoclinic crystalline form is preserved; each monoclinic crystal consists of an aggregate of minute crystals of rhombic sulfur. At lower temperatures the rate of transition becomes much slower. Ordinary roll sulfur or brimstone and flowers of sulfur consist principally of the rhombic form together with some amorphous sulfur.

Low-temperature studies on the two crystalline forms of sulfur have been made by Eastman and McGavock. The following table contains representative results of their measurements on the atomic heat capacities.

TABLE 70
THE HEAT CAPACITIES OF SULFUR

T (°K)	C_p, Rhombic	C_p, Monoclinic	T (°K)	C_p, Rhombic	C_p, Monoclinic
15	0 311	—	100	3.060	3.100
20	.605	—	140	3.795	3.882
30	1.075	—	200	4.639	4.798
50	1.772	—	260	5.154	5.371
60	2.084	2.091	300	5.412	5.662
80	2.604	2.624	360	5.783	6.069

The atomic entropies of the two forms obtained from the low-temperature experiments are $S^\circ_{298.1}$ (rhombic) = 7.624 cal/deg, $S^\circ_{368.6}$ (rhombic) = 8.827 cal/deg, $S^\circ_{298.1}$ (monoclinic) = 7.78 cal/deg, $S^\circ_{368.6}$ (monoclinic) = 9.04 cal/deg. From these results one may calculate the entropy change at 95.5° attending the transition S (rhombic) = S (monoclinic), $\Delta S^\circ_{368.6} = 0.21$. We should obtain the same result from a knowledge of ΔH at the transition temperature, since $\Delta S = \Delta H/T$; actually $\Delta S = 95/368.6 = 0.26$, and within the experimental error this agrees with the third law result.

Both rhombic and monoclinic sulfur are soluble in carbon bisulfide and other organic solvents, the monoclinic form being 1.28 times as soluble as the rhombic at 25.3° and 1.40 times as soluble at 0° in nearly all

ents [Brönsted, *Z. phys. Chem.*, **55**, 371 (1906)]. Both forms in
on bisulfide solution have a molecular weight corresponding to S_8.
solubility of rhombic sulfur in 100 g of CS_2 is 50.4 g at 25°, 100.0 g
0°, and 376.1 g at 80°; at −80° the content of rhombic sulfur in a
rated solution is 2.53% by weight.

Sulfur monochloride, S_2Cl_2, is also a very good solvent for sulfur of
er the rhombic or monoclinic form. One hundred g of benzol dis-
es about 2 g of sulfur at 25°. The following solubilities, S_m and S_r, in
ns per 10.0 cc of solution are due to Brönsted.

Table 71
SOLUBILITY OF SULFUR IN VARIOUS SOLVENTS

Solvent	Temp. (°C)	S_m, Monoclinic	S_r, Rhombic	Ratio S_m/S_r
zol	18.6	0.2004	0 1512	1.32
	25.3	.2335	.1835	1.27
roform	0	.1101	.0788	1.40
	40	.29	.24	1.2
er	0	.0113	.0080	1.41
	25.3	.0256	.0200	1.28
yl bromide	0	.0852	.0611	1.40
	25.3	.1676	.1307	1.28
yl formate	0	.0028	.0019	1.4
hol (ethyl)	25.3	.0066	.0052	1.3

Rhombic sulfur melts, if heated rapidly, at 112.8°, and the fact that
point can be attained is due to the slowness of the transition from
mbic to monoclinic sulfur. The monoclinic sulfur melts at 119.0°,
the "natural" melting point is a few degrees lower; this difference is
to the fact that liquid sulfur at equilibrium is a mixture of two or
ee molecular species, S_λ, S_μ, and S_π (or S_8, S_6, and S_4), and some time is
uired for the equilibrium between them to be attained. The liquid
se resulting from the rapid melting of rhombic or monoclinic sulfur
sists of S_λ.

Sulfur at 120° is a clear yellow liquid. If the temperature of the
id is increased, it becomes more and more viscous up to 165–200°, and
n the viscosity decreases until at the boiling point, 444.60°, the liquid
gain mobile. If the boiling liquid is poured into water, it forms a soft
ky mass or threads known as "plastic sulfur." This plastic material
dens with time: the higher the temperature at which it is held, the
rter the time required for the hardening (1 hour at 100°, several days
25°). When treated with carbon bisulfide, only a part of this hard-
d sulfur will dissolve; the insoluble material is known as S_μ, the solu-
part as S_λ. The equilibrium proportion of S_μ in liquid sulfur depends
its temperature. By means of carbon bisulfide extraction experi-

ments on the solid that eventually results from the rapid cooling of the liquid, the following proportions of S_μ have been found [see Lewis and Randall, *J. Am. Chem. Soc.*, **33,** 476 (1911), for a discussion of the experiments of Alexander Smith]:

TABLE 72
THE FRACTION OF S_μ IN LIQUID SULFUR

Temperature of Liquid (°K)	Fraction of S_μ	Temperature of Liquid (°K)	Fraction of S_μ
393	0.040	473	0.270
423	.067	573	.332
443	.187	718	.341

In addition to S_λ and S_μ, still another molecular species of sulfur, S_π, is believed to exist both in the liquid and in the rapidly cooled solid; Table 72 does not take account of this third kind of sulfur, it being lumped together with S_λ. A study of the third form, S_π, was made by Aten [*Z. phys. Chem.*, **86,** 1 (1914); see also Aten, *Z. phys. Chem.*, **88,** 321 (1914)], who observed that the solubility in carbon bisulfide and toluol at −80° of what was formerly known simply as S_λ depends on the temperature of the liquid sulfur before chilling in cold water. He established the solubility relations at −80° in the two solvents—for example, the per cent by weight, P_π, of S_π in a saturated solution in carbon bisulfide at −80° is given by $P_\pi = -2.24 + 0.88P_\iota$, where P_ι is the per cent of total sulfur in the saturated solution and is never less than 2.53%—and made use of the results in the analysis of the suddenly chilled liquid sulfur. His final results for the composition of molten sulfur, at equilibrium, for a number of temperatures are as follows:

TABLE 73
PERCENTAGE COMPOSITION OF LIQUID SULFUR AT EQUILIBRIUM

Temperature (°C)	S_μ (Per Cent)	S_λ (Per Cent)	S_π (Per Cent)
120	0.1	96.4	3.5
130	.3	95.4	4.3
140	1.3	93.7	5.0
160	4.1	89.2	6.7
170	13 3	80.9	6.8
180	20 4	73.1	6.5
196	28 6	65.1	6.3
220	32.2	62.7	5.3
445	36.9	59.1	4.0

It is noteworthy that the concentration of S_π goes through a maximum at about 170°; it is in this range that the viscosity of the liquid is greatest.

The amount of S_μ found depends somewhat on the rapidity of cooling; more rapid cooling from higher temperatures leads to a slightly higher percentage of S_μ [Hammick, Cousins, and Langford, *J. Chem. Soc.*, 797 (1928)].

Still another form of sulfur, S_ρ, is known and is obtained by extracting an acidified sodium thiosulfate solution with toluol. Molecular weight determinations in boiling carbon bisulfide lead to the following formulas for the known forms of sulfur [see Aten, *Z. phys. Chem.*, **88**, 321 (1914)]:

S (rhombic)	S (monoclinic)	S_λ	S_ρ	S_π
S_8	S_8	S_8	S_6	S_4

The melting points of S (rhombic), 112.8°, and S (monoclinic), 119°, given above refer to the change in state $S(s) = S_\lambda$. If equilibrium between S_λ, S_μ, S_π and the solid phase is established, then the "natural" melting points of rhombic and monoclinic sulfur are lower, namely, 110.4° and 114.6°, respectively. The observed melting points are ordinarily carried out rapidly and before the equilibrium $S_\lambda = S_\mu$ has time to be established; the reaction $S_\lambda = S_\mu$ is not a rapid one. It is of interest that the rate of the conversion $S_\lambda = S_\mu$ is greatly increased if NH_3 is bubbled through the liquid. The catalytic effect is so great that, when the liquid sulfur is cooled rapidly by pouring it on ice, only S_λ is obtained. If the treatment with NH_3 is followed by treatment with SO_2, the rate of $S_\lambda = S_\mu$ again becomes very slow, and the rapidly cooled liquid contains the equilibrium amount of S_μ. In these mixtures S_π is also present; ammonia and sulfur dioxide appear to act catalytically in the same way on S_π as on S_μ.

A number of X-ray investigations of liquid and plastic sulfur have been made with somewhat divergent results. Probably the most reliable study to date is that of Gingrich [*J. Chem. Phys.*, **8**, 29 (1940)]. From radial distribution curves he found that in plastic sulfur each atom has 2.0 nearest neighbors at 2.08 Å distance. Liquid sulfur was investigated at temperatures from 124° to 340°. The observed peaks on the microphotometer trace of the film were observed to shift somewhat with temperature with a discontinuity at 157–166°, roughly the temperature of maximum viscosity, but radial distribution curves gave for all temperatures 1.7 nearest neighbors at 2.08 Å within experimental error. A possible interpretation of the 1.7 is that the original S_8 ring is opened. This would give each sulfur an average of 1.75 nearest neighbors. However, this figure could be derived from a number of possible complex mixtures of chains and rings; and the exact structure of neither plastic nor liquid sulfur can be regarded as completely understood.

The boiling point of sulfur is fixed, on the international temperature scale, at 444.60°. The technique involved in attaining this fixed temperature has been investigated very carefully by Beattie, Blaisdell, and

Kaminsky [*Proc. Amer. Acad. Arts and Sciences*, **71,** 327 (1937)]. The liquid-vapor equilibrium temperatures (condensation points) on the international scale are given in terms of the pressure in mm Hg by the empirical equation

$$t = 444.60 + 0.0908028(p - 760) - 0.000047573(p - 760)^2 + 0.00000004361(p - 760)^3$$

As a result of more careful measurements, it is found that the normal sulfur boiling point, 444.60° on the international scale, is about 0.1° lower than it would be on the true thermodynamic scale. The value 444.60° will continue to be accepted as the boiling point until the international committee meets to revise it.

Selenium

Selenium resembles sulfur in its ability to exist in several forms. The finely divided amorphous and the lump or vitreous selenium of commerce are dark red to black in color when large pieces are viewed; thin pieces of it are seen to be red by transmitted light. The lump or vitreous selenium exhibits a conchoidal fracture and, although harder, resembles brittle tar; it is ordinarily obtained by heating selenium above its melting temperature and then allowing it to cool. Vitreous selenium is not a single crystalline modification, but is a mixture in the same sense that $S_{\lambda,\mu}$ is. If these forms of selenium are kept at 150° for several hours, they transform into the hexagonal crystalline form.

The hexagonal form is metallic in nature and is often designated as metallic selenium. In color it is gray with a metallic luster, and is accordingly also known as "gray selenium." Although it is not absolutely certain that it is the stable form at 25°, there is some reason for believing that it is. It is insoluble in carbon bisulfide, and is a conductor of electricity. The electrical conductivity of the metallic form is from three to as much as 200 times as great in the light as in the dark. Light of 7000 Å wave length appears to be most effective in increasing the conductivity. In general, the conductivity is roughly proportional to the cube root of the light intensity and to the logarithm of the applied potential [Barton, *Phys. Rev.*, **23,** 337 (1924); Gudden and Pohl, *Phys. Z.*, **22,** 529 (1921); Fournier de Albe, *Proc. Roy. Soc.*, **89,** 75 (1913)]. The method of preparation and small amounts of impurity affect the resistance sensitivity to light. The melting point of the hexagonal or metallic form of selenium is 217.4°.

When amorphous selenium, such as that obtained when H_2SO_3 reduces H_2SeO_3 solutions, or vitreous selenium is extracted with carbon bisulfide, some, but not all, of it dissolves to give amber to ruby-red colored solutions. If these solutions are evaporated slowly below 72°, red, monoclinic crystals known as alpha monoclinic selenium are deposited. If the solvent is vaporized at 75° or above, hexagonal selenium results. Rapid evaporation or cooling of saturated solutions yields still another red monoclinic form known as beta monoclinic selenium. The beta form will dissolve in a carbon bisulfide solution saturated with the alpha form. When placed in quinoline at 25°, both the alpha and beta monoclinic forms are transformed slowly into the hexagonal form. This fact shows that, although a higher temperature, 75 to 150°, is required to convert dry monoclinic to hexagonal selenium, the hexagonal form is actually the more stable form at the lower temperatures. The rates at which the dry monoclinic seleniums are converted into the hexagonal form are extremely slow at room temperatures. In the presence of solvents and hexagonal crystals, the monoclinic forms will go over into the hexagonal form at room temperature (McCullough, "A Study of the Allotropes of Selenium," Thesis, Cal. Inst. Tech., 1936. X-ray methods were used in this study).

The densities of hexagonal, alpha monoclinic, and beta monoclinic selenium are 4.86, 4.46, and 4.42, respectively, at room temperature. The solubilities of the alpha and beta monoclinic modifications in carbon bisulfide are not known but have been estimated as .05% by weight of solution. Their melting points, if rapidly heated, are around 170–180°.

Less is known about liquid selenium than about liquid sulfur. In a qualitative manner, the properties of molten selenium are similar to those of molten sulfur: there is reason to believe that the former, like the latter, consists of two or more molecular species; however, the viscosity decreases steadily with increase in temperature [*Chem. Abst.*, **31**, 6072 (1937)]. In a study by Briegleb [*Z. phys. Chem.*, **144**, 321, 350 (1929)], molten selenium was rapidly chilled by pouring it on finely divided ice cooled to −180°; the resulting solid was then extracted with carbon bisulfide until all soluble selenium was removed. No catalysts, negative or positive, were found that would affect the rate of the apparently rapid transformations taking place in the liquid. Consequently, the final results are not as certainly a representation of the true equilibrium state of the liquid as is the case with sulfur. The following table shows the per cent of soluble selenium in the liquid at various temperatures. Since liquid selenium may be strongly supercooled, results were obtained for temperatures below the melting point.

t (°C)	Per Cent Soluble Se in Se(l)	t (°C)	Per Cent Soluble Se in Se(l)
120	55	500	18
220	41	600	15
300	30	650	14
400	23		

A careful investigation of the boiling point (condensation point) of purified selenium at various pressures near atmospheric was made by M. de Selincourt [*Proc. Phys. Soc.* (London), **52,** 348 (1940)], who found for 760.0 mm pressure, b.p. = 684.8° ± 0.1°, on the international temperature scale. The b.p. changes by 1.08° per cm change in pressure.

Tellurium

Tellurium differs from selenium more than the latter does from sulfur. Sulfur is a nonmetal; selenium has common nonmetallic forms as well as the stable metallic form; tellurium is definitely a metal in appearance and, moreover, does not exhibit markedly nonmetallic forms. The stable crystalline form of tellurium is hexagonal-rhombohedral. It is silvery white in appearance, and has a density of 6.19 to 6.24 g/cm³. Sticks of the metal are very brittle and not very hard. There is some indication that the finely divided brown form, obtained when solutions of TeO_2 are reduced with H_2SO_3, is nonmetallic and amorphous.

The metallic or common form melts at 449.8° ± 0.2°, and the liquid boils at 1390° [Kracek, *J. Am. Chem. Soc.*, **63,** 1989 (1941)].

The vapor states of S, Se, and Te

The vapor molecules of sulfur, selenium, and tellurium show a marked tendency to exist in several polymeric forms, a characteristic exhibited to a much lesser extent by oxygen. In sulfur vapor, the molecules S, S_2, S_6, and S_8 are believed to be in equilibrium with each other. At room temperatures S_8 predominates and, at some 800°, S_2. At still higher temperatures the concentration of monotomic sulfur becomes appreciable. Because the vapor consists of several molecular species, vapor-pressure formulas are not as significant as they would otherwise be, since, for most thermodynamic calculations one would wish to know the partial pressure of each molecular species in equilibrium with the solid or liquid. In order to calculate these quantities, not only the total vapor pressure, but also the equilibrium constants involved are necessary. In the following Table 74 are presented representative values for vapor pressures together with other physical data for S, Se, and Te [Preuner and Schupp, *Z. phys. Chem.*, **68,** 129 (1909); Preuner and Brockmöller, *ibid.*, **81,** 129 (1912); Dodd, *J. Am. Chem. Soc.*, **42,** 1579 (1920); Doolan and Partington, *Trans. Faraday Soc.*, **20,** 342 (1924); Anderson, *J. Am. Chem. Soc.*, **59,** 1036 (1937); Eastman and Gavock, *J. Am. Chem. Soc.*, **59,** 145 (1937); Neumann, *Z. phys. Chem.*, **171A,** 416 (1934); Slansky and Coulter, *J. Am. Chem. Soc.*, **61,** 564 (1939)]. Recent electron-diffraction studies have shown that the S_8 molecule is a regular puckered ring with $S - S = 2.07$ Å and $\angle S - S - S = 105° \pm 2°$ [C. S. Lu and J. Donohue, *J. Am. Chem. Soc.*, **66,** 818 (1944)].

The formulas at the bottom of the table may be used to show that, at the temperatures above 440°K, the proportion of S_2 in sulfur vapor is greater than that of Se_2 in selenium vapor. Below 440°K the reverse is true. It will be noted that no information is given in the table concerning Se_8. It is believed that Se_8 exists at lower temperatures; but, at the temperatures where measurements are possible, Se_8 is extensively decomposed into Se_6 and Se_2. Vapor-density measurements on tellurium are possible only at quite high temperatures. From 1400° to 2100° the measurements indicate that the gas consists of Te_2 molecules. Electron-diffraction experiments on tellurium vapor at roughly 600° show that mainly Te_2 molecules are present.

The experiments that were made to establish the nature of the vapors of sulfur and selenium vapor consisted essentially of vapor-

TABLE 74

THE PHYSICAL PROPERTIES OF S, Se, AND Te

	Melting Point* (°C)	Boiling Point (°C)	Heat of Fusion at M.P. (cal)§	Heat of Vaporization (cal)†	Atomic Entropy of Solid, S°_{298} (cal/deg)
S.	118.95	444.60	350	29,100 (S_2, 18°)	7.624 (r) 7.78 (m)
Se. .	217.4	684.8	1600	29,500 (Se_2, 18°)	10.0
Te . . .	449.8	1390.	4270	24,000 (Te_2, 18°)	11.88

* The liquid phase consists of S_λ in the case of S. The information on Se (l) and Te (l) is not complete.

§ For one atomic weight of the element.

† For 8S (rhombic) = S_8 (g), $\Delta H^\circ = 24{,}080$ cal

8S (monocl.) = S_8 (g), $\Delta H^\circ = 23{,}240$ cal

S (monocl.) = S (rhombic), $\Delta H_{368.6}^\circ = 95$ cal

Vapor Pressures

S (Rhombic)		S (Monoclinic)		S(l)	
t (°C)	$p_{mm} \times 10^4$	t (°C)	$p_{mm} \times 10^4$	t (°C)	p_{mm}
60	1.0	95.5	37.5	120	0.040
70	3.2	96.2	40	190	1.4
79.9	8.9	103.8	75	260	16.0
88.9	20.7	111.6	141	330	95.0
95.5	37.5	115.4	192	400	376
				444.60	760.0

TABLE 74. (*Cont.*)

Se		Te	
t (°C)	p_{mm}	t (°C)	p_{mm}
217.4	0.0055	488	0.464
220	0.0062	578	3 34
235	0.012	671	14 1
390	3 0	1390	760
480	28 0		
620	313 0		
680	760.0		

$$S_6(g) = 3S_2(g), \qquad K = \frac{p^3_{S_2}}{p_{S_6}}, \qquad \log_{10} K_{mm} = -\frac{14{,}542}{T} + 21.907$$

$$S_8(g) = 4S_2(g), \qquad K = \frac{p^4_{S_2}}{p_{S_8}}, \qquad \log_{10} K_{mm} = -\frac{21{,}348}{T} + 32.910$$

$$Se_6(g) = 3Se_2(g), \qquad K = \frac{p^3_{Se_2}}{p_{Se_6}}, \qquad \log_{10} K_{mm} = -\frac{13{,}000}{T} + 18.40$$

density measurements, and in the interpretation of the results, each molecular species was assumed to act as a perfect gas, an assumption that is doubtless justified since the temperatures employed were moderately high [Preuner and Schupp, Preuner and Brockmöller, *loc. cit.*]. It must be pointed out that, without detracting in the least from the excellent experimental results on S and Se vapors, the measurements may be interpreted on the basis of polymers other than those assumed. In fact, all equilibrium measurements that involve sulfur and selenium vapors do not hang together in a satisfactory manner. It may well be that some other interpretation of the vapor-density measurements would be in better accord with other measurements involving sulfur and selenium vapors.

TABLE 75

THE MOLAL PARAMAGNETIC SUSCEPTIBILITY OF S_2(g)

t (°C)	$\chi_m \times 10^4$	$\chi_m T$
590	8.3	0.72
650	8.1	75
725	7.3	.73
760	5.7	.59
800	5 4	.58

Both solid and liquid sulfur are diamagnetic, but the vapor is paramagnetic. These facts would indicate that the S_2 molecule is responsible for the paramagnetism, since liquid sulfur, $S_{\lambda\mu\pi}$, consists of S_8, S_6, and S_4 and is diamagnetic. Representative values of the molal susceptibilities of S_2 are given in Table 75 [Neel, *Compt. rend.*, **194,** 2035 (1932)]. In calculating the values of χ_m from the measurements account was taken of the concentration of S_2 in the sulfur vapor.

The theoretical value of $\chi_m T$ would be 1.00 if two electron spins were responsible for the paramagnetism and 0.375 if only one were involved. Clearly, S_2 does not obey Curie's law exactly, and $\chi_m T$ is less than required by theory for two parallel electron spins. In spite of this difficulty it is believed that the ground state of S_2, like that of the oxygen molecule, is $^3\Sigma$, and that the lack of agreement between theory and experiment is to be ascribed to experimental difficulties or to lack of accurate knowledge of the kinds of molecules in sulfur vapor. Qualitative experiments have shown selenium vapor to be paramagnetic [Bhatmager, Lessheim, and Khanna, *Proc. Ind. Acad. of Sci.*, **6A,** 155 (1937)]. No measurements are available on Te_2, but in analogy with oxygen and sulfur the ground states of these molecules are assumed to be $^3\Sigma$. The difference in energy between the triplet ground states is, as in oxygen, small.

Sulfur, selenium, and tellurium vapors show absorption bands in the ultraviolet and visible region of the spectrum, and the fluorescent spectra of selenium and tellurium can be excited by radiation from the mercury arc. Studies made by both methods have led to the energy states of the S_2, Se_2, and Te_2 molecules given in Table 76 [Herzberg, *Molecular Spectra,* pp. 492, 494]. The interpretation of the rotational or fine structure of the S_2 absorption bands is still subject to some doubt; indeed, it is not certain but that impurities are responsible for some of the bands observed.

TABLE 76

VIBRATIONAL ENERGY STATES OF S_2, Se_2, AND Te_2

S_2 $\epsilon_{vib.}/hc = 725.8(v + \frac{1}{2}) - 2.85(v + \frac{1}{2})^2$ cm^{-1}
S—S distance, 1.89 Å[a], 1.92 Å[b]
Se_2 $\epsilon_{vib.}/hc = 391.77(v + \frac{1}{2}) - 1.06(v + \frac{1}{2})^2$ cm^{-1}
Se—Se distance, 2.16 Å[a], 2.19 Å[b]
Te_2 $\epsilon_{vib.}/hc = 251.5(v + \frac{1}{2}) - 1.0(v + \frac{1}{2})^2$ cm^{-1}
Te—Te distance, 2 59 Å[b]

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[a] Spectroscopic value [Herzberg, *Molecular Spectra*].

[b] Electron-diffraction value [Maxwell, Hendricks, and Moseley, *Phys. Rev.*, **49,** 199 (1936); **57,** 21 (1939)].

The entropies of gaseous S_2, Se_2, and Te_2 may be calculated from the data in Table 76; they are given in Table 77 together with the heats of dissociation of the molecules [Herzberg, *loc. cit.*]. An uncertainty in the heat of dissociation of S_2 prevents accurate calculation of the equilibrium constant for the reaction $S_2(g) = 2S(g)$. Values based on a heat of dissociation of 83,000 cal/mole and the free-energy functions of Montgomery and Kassel [*J. Chem. Phys.*, **2,** 417 (1934)] are given in the table.

The rather detailed consideration that has been given to the oxygen group elements O, S, Se, and Te is in keeping with their importance. Many of the general properties that they exhibit are much like those observed in such elements as phosphorus, sodium, carbon, and many others. They exist in several crystal modifications, the liquids do not consist of a single molecular species, and their vapors consist of polymers in equilibrium with each other. Although a chemist is more frequently interested in the reactions between compounds than in the elements themselves, the latter are of interest in that they show rather simply characteristics that are fundamentally the same in compounds but more complicated in nature. The problems encountered in the elementary substances just discussed involve three main factors common to all chemical studies, namely, reaction rates, equilibria, and molecular structure.

TABLE 77

THERMODYNAMIC CONSTANTS OF S_2, Se_2, AND Te_2

The Dissociation of S_2

	Heat of Dissociation at 0°K (cal/mole)	Entropy of Gas, $S^\circ_{298.1}$ (cal/deg/mole)
S_2	83,000	54.42
Se_2	62,300	60.3
Te_2	53,100	64.1

$$S_2(g) = 2S(g)$$

T (°K)	$\log_{10} P_S^2/P_{S_2}$*	T (°K)	$\log_{10} P_S^2/P_{S_2}$*
298.1	−55.9	2000	−2.9
600	−24.7	3000	+0.26
1000	−12.3	5000	+2.8

* The pressures P are expressed in atmospheres.

Hydrogen Sulfide, Selenide, and Telluride

Preparation and properties

For most experimental purposes H_2S, H_2Se, and H_2Te are best prepared by the action of acids on metal sulfides, selenides, and tellurides. Thus the reactions of FeS, FeSe, Al_2Se_3, MgSe, and Al_2Te_3 with dilute (6 n) hydrochloric acid or water (FeS requires acid; FeSe requires acid and warming) yield H_2S, H_2Se, and H_2Te. In order to avoid such impurities as AsH_3, synthesized sulfides are preferred to the naturally occurring FeS. Another method of preparation consists in heating mixtures of S or Se with paraffin, naphthalene, or resins. This method has found application in one step in the manufacture of selenium cells, the H_2Se being decomposed to form hexagonal selenium when it comes in contact with a heated plate to be used in the cell. H_2Te (but not, with good yields, H_2S or H_2Se) may be prepared by the electrolysis of 50% H_2SO_4 or H_3PO_4 solutions with metallic tellurium as a cathode.

The hydrolytic processes of preparation depend on the fact that all three hydrides are weak acids and volatile. Acids are not always necessary for the hydrolysis of metal sulfides; the compounds BaS and CaS react with water or water vapor to form H_2S and the metal hydroxides or oxides. The conversion is not always complete where solutions are involved, since much $S^{=}$ or HS^{-} may be present but only a very small amount of H_2S; for example, solutions of Na_2S and NaHS have very little odor of H_2S above them. The hydrolytic reactions in alkaline solutions come to equilibrium before much H_2S is formed, less and less H_2S being found with increasing alkalinity. Al_2Se_3, MgSe, and Al_2Te_3 yield H_2Se and H_2Te with water alone, although in one method of preparation the powdered material is dropped into 4 n hydrochloric acid. In the method employing the action of steam on FeS, the reaction, $FeS + H_2O = FeO + H_2S$, is reversible; but the removal of the product results in complete conversion of the metal sulfide to hydrogen sulfide.

The direct combination of the elements has been studied repeatedly with respect to both the rate and the equilibrium state. Qualitatively it may be said that S and Se will react with hydrogen directly, very slowly at ordinary temperatures and more rapidly at high temperatures, but H_2Te is so unstable thermodynamically that its direct synthesis at

TABLE 78

THE PHYSICAL, THERMODYNAMIC, AND STRUCTURAL PROPERTIES OF H_2S, H_2Se, AND H_2Te

	Melting Point (°C)	Heat of Fusion (cal)	Boiling Point (°C)	Heat of Vaporization (cal)
H_2S	−85.49	568.1	−60.33	4,463
H_2Se	−65.9	—	−41.2	4,760
H_2Te	−57.	—	0.0	5,700

	Heat of Formation, ΔH (cal)	Free Energy of Formation, ΔF°_{298} (cal)	Standard Entropy, S°_{298} (cal/deg)
H_2S	−4,800 (25°)	−7,865	49.15
H_2Se	18,500 (18°)	2,370	53.
H_2Te	34,200 (18°)	31,000	56.

H_2S

$$H_2(g) + S_2(g) = H_2S(g) \qquad \Delta E_0^\circ = -19{,}620 \text{ cal}$$

$$\Delta F_T^\circ = -19{,}200 + 0.94T \log_e T + 0.00165T^2 - 3.7 \times 10^{-7}T^3 + 1.65T$$

TABLE 78 (*Cont.*)

Moments of inertia:

$I_1 = 2.667 \times 10^{-40}$, $I_2 = 3.076 \times 10^{-40}$, $I_3 = 5.845 \times 10^{-40}$ g cm^2

$\omega_1 = 1260$ cm^{-1} $\omega_2 = \omega_3 = 2620$ cm^{-1}

T (°K)	C_p (cal/deg)	$S°$ (cal/deg)	T (°K)	C_p (cal/deg)	$S°$ (cal/deg)
298.1	8.121	49.151	1000	10.85	60.25
500	8.81	53.50	1400	11.94	64.09
700	9.67	56.60	1800	12.58	67.17
900	10.49	59.13			

H_2Se

$H_2(g) + Se_2(g) = H_2Se(g)$ $K = \dfrac{p_{H_2Se}}{p_{H_2}p_{Se_2}}$ $\omega_1 = 1074$ cm^{-1}

t (°C)	600	700	800
K_{mm}	37	150	500

$\omega_2 = 2260$ cm^{-1}

$\omega_3 = 2350$ cm^{-1}

$H_2(g) + Se(l) = H_2Se(g)$ $K = \dfrac{P_{H_2Se}}{P_{H_2}}$

t (°C)	K_{atm}	t (°C)	K_{atm}	t (°C)	K_{atm}
254	0.162	324	0.292	405	0.439
274	.205	356	.350	444	.515
301	.258	377	.398	493	.605

$H_2Se(g) + I_2(s) = 2HI(g) + Se$ (amorph.), $\Delta H = 3945$ cal

T (°K)	K_{atm}
273.1	33.68
290.1	22.62
300 0	18.06

readily attainable temperatures is out of the question. The rate of the reaction $H_2(g) + S(g) = H_2S(g)$ in the presence of liquid sulfur is measurable in the range 265–340°, but the measurements do not admit of a satisfying interpretation; in part the reaction is heterogeneous and in part homogeneous, the rate of the former predominating [Norrish and Rideal, *J. Chem. Soc.*, **125**, 2070 (1924); Kassel, *Kinetics of Homogeneous Gas Reactions*, p. 159]. The reaction $H_2 + Se = H_2Se$ is also very slow below about 250°.

In Table 78 are presented data on equilibrium measurements on H_2S and H_2Se, as well as on other important physical properties [Preuner and

Brockmöller, *Z. phys. Chem.*, **81**, 129 (1912); Bodenstein, *ibid.*, **29**, 429 (1899); I. C. T., Vol. V; Cross, *J. Chem. Phys.*, **3**, 168 (1935); Nielsen and others, *ibid.*, **7**, 994 (1939); Bichowsky and Rossini, *Thermochemistry;* Kelley, *Bureau of Mines Bull.*, **406**, p. 18 (1937); Giauque and Blue, *J. Am. Chem. Soc.*, **58**, 831 (1936)].

It is evident from the table that in an equilibrium mixture of H_2, Se_2, and H_2Se,* the amount of H_2Se increases with the temperature; in an equilibrium mixture of H_2, S_2, and H_2S, on the other hand, the amount of H_2S decreases with increasing temperature. The same conclusion is indicated by the heats of formation. Equilibrium measurements show that H_2S will decompose but very little at room temperature; H_2Se and H_2Te are unstable at room temperatures, but their rates of decomposition are slow, H_2Te decomposing more rapidly than H_2Se. The slow decomposition rates make it possible to carry out experiments with H_2Se and H_2Te, although they are thermodynamically unstable with respect to the elements.

Chemical properties

All of the sulfur-group hydrides are moderately and roughly equally soluble in water, and all ionize, but not completely, in this solvent. Solutions of H_2S are least acidic and those of H_2Te the most. The solubilities and ionization constants are given in Table 79 [Lewis and Randall,

TABLE 79
SOLUBILITIES IN WATER AND IONIZATION CONSTANTS OF H_2S, H_2Se, AND H_2Te AT 25°

	Solubility (moles/liter), $p = 760$ mm	IONIZATION CONSTANTS	
		$K_1 = \frac{(H^+)(HY^-)}{(H_2Y)}$	$K_2 = \frac{(H^+)(Y^=)}{(HY^-)}$
H_2S.....	0.102	1.15×10^{-7}	10^{-15}
H_2Se. ..	.08415	1.88×10^{-4}	$\approx 10^{-10}$
H_2Te...	Unknown, > 0.09	2.27×10^{-3} (18°)	$\approx 10^{-5}$

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* It must be noted that the values of K in the table for the reactions $H_2 + Se_2 = H_2Se$, $H_2 + Se(l) = H_2Se$, and $Se_6 = 3Se_2$ are not consistent with each other. The reason for this is not known, but may involve the assumption of only Se_6 and Se_2 molecules in selenium vapor. There is also a difficulty with regard to the free energy of $H_2Se(g)$. The heat of formation given in the table combined with known and reasonably assumed entropy values lead to $\Delta F^\circ_{298} = 15{,}300$ cal for the reaction $H_2(g) + Se(s) = H_2Se(g)$ [Latimer, *Oxidation Potentials*, p. 75]. On the other hand the equilibrium constants for the reaction $H_2Se(g) + I_2(s) = 2HI(g) + Se(s)$ [Rolla, *Gazz. Chim.*, **42**, 432 (1912)] lead to a value $\Delta F^\circ_{298} = 2{,}370$ cal for the free energy of formation of $H_2Se(g)$. Here again the discrepancy is large and the reason for it is not evident. A reinvestigation of Rolla's reaction might settle the question.

Thermodynamics; McAmis and Felsing, *J. Am. Chem. Soc.*, **47,** 2633 (1925); Bruner, *Z. Electrochem.*, **19,** 861 (1913); Hlasko, *J. chim. phys.*, **20,** 167 (1923)].

The sulfur-group hydrides all react with oxygen and the halogens to form oxides, the elements themselves, and halides. H_2S reacts only slowly if at all with O_2 at room temperatures but will burn if ignited. It is thermodynamically stable at room temperatures and may be stored in liquid form in steel cylinders without difficulty. Dry H_2Se does not react with oxygen at room temperatures, but in the presence of moisture, water and elementary selenium are formed; the gas burns with a blue flame. H_2Te dry or moist reacts rapidly with oxygen with the formation of dark-colored deposits of Te. Dry and pure H_2Se and H_2Te can be kept for reasonable periods without decomposition; H_2Te is more sensitive to catalysts and decomposes more rapidly than does H_2Se. In aqueous solutions both H_2Se and H_2Te are readily oxidized by such weak oxidizing agents as Fe^{+++} and I_2. In solution H_2S is also fairly easily oxidizable, such agents as Fe^{+++}, I_2, and HVO_3 being able to liberate free sulfur quantitatively from it. As has been indicated in the preceding section, H_2Te is the strongest reducing agent and H_2S the weakest of the three analogous compounds.

The three sulfur-group hydrides, being acidic in nature, can combine with bases to form salts analogous to the hydroxides and oxides. When H_2S is passed into a solution of NaOH, there are formed NaSH and Na_2S, or, more precisely, HS^- and $S^=$. Owing to the weakness of the acid, the salts hydrolyze extensively, so that solutions of both NaHS and Na_2S are alkaline. The corresponding compounds of selenium and tellurium behave in a similar manner, the extent of hydrolysis not being so great, since H_2Se and H_2Te are stronger acids than H_2S.

Solutions of NaHTe (and H_2Te) are readily oxidized by oxygen, and, indeed, all of the tellurium can be liberated by passing air or oxygen through the solutions. Solutions of NaHSe are also oxidized by oxygen but not as rapidly. The effect of oxygen on NaHS solutions is noticeable, but the rate of liberation of sulfur to form polysulfides is fairly slow; unless air or oxygen is carefully excluded, the solutions soon become orange in color owing to the formation of polysulfide ions.

When S, Se, or Te are added to solutions of their *ide* salts, the polysulfides, selenides, or tellurides are formed. The composition of these substances depends upon the amount of the element added; that is, several ions are present together in equilibrium with each other, for example,

$$S^= + S = S_2^=$$
$$S^= + 2S = S_3^=$$
$$\cdots\cdots\cdots\cdots\cdots$$
$$S^= + 5S = S_6^=$$

and similarly for selenium and tellurium. The insecticide known as lime-sulfur, prepared by boiling together solutions of lime with sulfur, contains, among other sulfur compounds, calcium polysulfides. The polysulfides are orange to red, the polyselenides red to green, and the polytellurides lavender to dark red in color. When acidified, the polysulfides yield S, H_2S, the liquids H_2S_2 and H_2S_3, and doubtless compounds containing still more sulfur (see Chap. 11). The polyselenides and tellurides decompose into H_2Se and H_2Te and the elements when acidified, there being little or no evidence for the existence of hydrides analogous to H_2S_2 and H_2S_3.

When aqueous solutions of Na_2S, Na_2Se, and Na_2Te are evaporated, the solid salts result, but these are often of uncertain composition. The sulfur-group elements react readily with sodium dissolved in liquid ammonia to form the normal sulfides, selenides, and tellurides, and on the addition of still more S, Se, or Te the *poly* salts as well. Ammonia can be evaporated readily from these mixtures, leaving behind the solid salts. The polysulfides in aqueous solution react slowly with air or oxygen to form thiosulfate and sulfur; the same reactions are observed in liquid ammonia solutions. Sodium polyselenides and polytellurides in liquid ammonia solutions are oxidized slowly by oxygen with the formation of selenites, selenates, tellurites, and tellurates, respectively [McCleary and Fernelius, *J. Am. Chem. Soc.*, **56**, 803 (1934)], in addition to free Se and Te.

The polysulfides, selenides, and tellurides are the analogues of the peroxides and higher oxides. In spite of their many interesting properties, comparatively little highly accurate thermodynamic data have been obtained for them. Some of the free energies of formation in the following list are, accordingly, rough estimates or guesses, but are doubtless of she right order of magnitude [Latimer, *Oxidation Potentials;* Kasarnowtky, *Z. anorg. Chem.*, **128**, 15, 33 (1923)].

Ion	ΔF°_{298} kcal	Ion	ΔF°_{298} kcal	Ion	ΔF°_{298} kcal
$S^{=}$	23.42	$Se^{=}$	35.76	$Te^{=}$	42.3
$S_2^{=}$	23.1	$Se_2^{=}$	34	$Te_2^{=}$	38 75
$S_3^{=}$	22.4				
$S_4^{=}$	20 7				

Numerous studies have been made to determine the types of polysulfides, selenides, and tellurides that are capable of existing. Phase diagrams and solubility relations have furnished the most significant information. The fact that all three of the sulfur-group elements react readily with the alkali metals in liquid ammonia solution has simplified the preparation of some of the compounds. In the following list are shown the known compounds [see, *e.g.*, Bergstrom, *J. Am. Chem. Soc.*, **48,** 146 (1926); Kraus and Glass, *J. Phys. Chem.*, **33,** 984, 995 (1929); Kraus and Zeitfuchs, *J. Am. Chem. Soc.*, **44,** 2714 (1922); Klemm, Sodomann, and Langmesser, *Z. anorg. Chem.*, **241,** 281 (1939)]:

Na_2S	Na_2S_2		Na_2S_4	Na_2S_5	
Na_2Se	Na_2Se_2	Na_2Se_3	Na_2Se_4		Na_2Se_6
Na_2Te	Na_2Te_2		(Na_2Te_4)		Na_2Te_6
K_2S	K_2S_2	K_2S_3	K_2S_4	K_2S_5	K_2S_6
K_2Se	K_2Se_2	K_2Se_3	K_2Se_4	K_2Se_5	
K_2Te					
Rb_2S	Rb_2S_2	Rb_2S_3	Rb_2S_4	Rb_2S_5	Rb_2S_6
Rb_2Se					
Rb_2Te					
Cs_2S	Cs_2S_2	Cs_2S_3	Cs_2S_4	Cs_2S_5	Cs_2S_6
Cs_2Se					
Cs_2Te					

A liquid ammonia solution of sodium sulfide or selenide saturated with sulfur or selenium contains at least some Na_2S_6 or Na_2Se_6. With tellurium the saturated solution contains Na_2Te_4 (or a mixture of Na_2Te_2 and Na_2Te_6); the higher telluride is obtained by melting a mixture of Na_2Te and Te of the proper composition. When S, Se, or Te is slowly added to a liquid ammonia solution of an alkali metal, the insoluble *ide* salt, for example K_2Te, K_2S, is formed first; but, with further addition of S, Se, or Te, the precipitate dissolves to form highly and beautifully colored solutions of the poly salts.

CHAPTER 9

The Halides and Oxyhalides of Sulfur, Selenium, and Tellurium

The Halides of Sulfur, Selenium, and Tellurium

Preparation

Sulfur, selenium, and tellurium combine directly with fluorine with considerable evolution of heat to form the following compounds: the hexafluorides SF_6, SeF_6, and TeF_6 in greatest proportions; S_2F_{10}, Se_2F_{10}(?), and Te_2F_{10} in small proportions. These substances are gases or volatile liquids. Sulfur hexafluoride is a remarkably unreactive gas that does not hydrolyze even in boiling water, although there is a strong thermodynamic tendency for it to do so. S_2F_{10} is also quite unreactive [Denbigh and Whytlaw-Gray, *J. Chem. Soc.*, 1346 (1934)]. Selenium hexafluoride hydrolyzes slowly in water to form HF and H_2SeO_4; tellurium hexafluoride hydrolyzes slowly, but at a rate greater than that for SeF_6. SeF_6 does not react with gaseous ammonia (or hydrogen) at room temperatures, but does so at 200°, with the formation of Se and HF. Both SeF_6 and TeF_6 react with mercury at room temperatures, the products of the reduction being HgF, Se, Te, and possibly mercury selenide [Yost and Claussen, *J. Am. Chem. Soc.*, **55**, 885 (1933); Klemm and Henkel, *Z. anorg. Chem.*, **207**, 73 (1932)].

By the action of HF on the oxides, or cobaltic fluoride, CoF_3, on the elements, compounds of the formulas S_2F_2 [Centnerszwer and Strenk, *Ber.*, **58**, 914 (1925); Trautz and Ehrmann, *J. prakt. Chem.*, **142**, 79 (1935)], SF_2, SF_4(?), Se_2F_2, SeF_4, TeF_2, and TeF_4 have been prepared, some in a fairly pure state, others definitely admixed with more or less impurities. Some uncertainty is felt by Sidgwick regarding the existence of SF_4 [Fischer and Jaenecker, *Z. angew. Chem.*, **42**, 810 (1929); Sidgwick, *Annual Reports*, Chemical Soc. Lond., 126 (1933)], but the reasons advanced for its nonexistence depend on the assumption of an "inert pair" of electrons in sulfur, and are not altogether convincing.

Chlorine and bromine, but not iodine, react readily with sulfur to form the liquids sulfur monochloride, S_2Cl_2 (yellow), and bromide, S_2Br_2 (red), of which only the former is capable of dissolving appreciable quantities of sulfur. Chlorine reacts slowly and reversibly with S_2Cl_2 to form the red, liquid dichloride SCl_2 [Lowry and Jessop, *J. Chem. Soc.*, 323 (1931); Spong, *J. Chem. Soc.*, 1283 (1934) *et ante;* see also Aten, *Z. phys. Chem.*, **54,** 55 (1905)]; at room temperature and with chlorine at atmospheric pressure the dichloride forms, but at about 100° the dichloride decomposes extensively into the monochloride and chlorine. It is believed that S_3Cl_4 is also present in the equilibrium mixture.

At $-30°$ or lower the action of Cl_2 on S, S_2Cl_2, or SCl_2 leads to sulfur tetrachloride, SCl_4, a liquid which freezes to a solid melting at $-31°$. When SCl_4 is at temperatures above the melting point, the equilibrium pressure of the Cl_2 exceeds one atmosphere; the reaction

$$SCl_2(l) + Cl_2(g) = SCl_4(l)$$

is reversible. At atmospheric pressure and room temperature SCl_4 does not exist [see, *e.g.*, Lowry and Jessop, *J. Chem. Soc.*, 1421 (1929); 782 (1930)]. The higher bromides do not appear to exist.

Selenium reacts readily with chlorine or bromine (and, under some conditions, iodine) to form the monochloride or bromide; these are dark red liquids having the formulas Se_2Cl_2 and Se_2Br_2 (and Se_2I_2). Both Se_2Cl_2 and Se_2Br_2 are excellent solvents for selenium. Further addition of chlorine to the monochloride yields the white, solid tetrachloride, $SeCl_4$; and with bromine the orange-red, solid tetrabromide, $SeBr_4$, is formed. The tetrachloride sublimes readily, but the vapor consists of a mixture of $SeCl_2$ and Cl_2 but not $SeCl_4$. Selenium tetrabromide can also be vaporized without difficulty, the vapor consisting of $SeBr_2$ and Br_2. So far as is known, the dichloride and dibromide exist only as gases; a liquid mixture whose composition corresponds to $SeCl_2$ appears to consist of the monochloride and crystals of the tetrachloride.

When a carbon tetrachloride solution of iodine is shaken with selenium, some of the selenium dissolves to form Se_2I_2 in the solution. A similar behavior is observed if the solvent is ethylene bromide, both Se_2I_2 and SeI_4 being formed in the solution. There is no convincing evidence for the existence of solid Se_2I_2 or SeI_4.

Tellurium does not form compounds analogous to S_2Cl_2 and Se_2Cl_2. It does react with the halogens to form the solid dihalides $TeCl_2$, $TeBr_2$, and TeI_2. Tellurium dichloride and dibromide may be melted and vaporized, the vapors having a violet color not easily distinguished from that of iodine vapor. The absorption spectra of $TeCl_2(g)$ and $TeBr_2(g)$ in the visible region consist of many well-defined bands, which have not, however, been subjected to analysis. Tellurium reacts with excess chlorine and bromine to form the solid tetrahalides $TeCl_4$ and $TeBr_4$. These substances boil at 414° and 421°, respectively; the gaseous tetrachloride begins to decompose reversibly into $TeCl_2(g)$ and Cl_2 to a measurable extent at 500°. $TeBr_4(g)$ at 740 mm total pressure is 90% decomposed into $TeBr_2$ and Br_2 at 432° [Simons, *J. Am. Chem. Soc*, **52.**, 3488 (1930); Yost and Hatcher, *ibid.*, **54,** 151 (1932)]. Tellurium tetraiodide is known as a solid, but in the vapor state and at 400° it will doubtless be completely dissociated into $TeI_2(g)$ and I_2.

All of the chlorides and bromides of sulfur, selenium, and tellurium react with water, some—S_2Cl_2, Se_2Cl_2, and Se_2Br_2—slowly, and others—$SeCl_4$, $TeCl_2$, $TeCl_4$, $TeBr_2$, and $TeBr_4$—rapidly. The types of hydrolytic reactions are as follows:

$$\begin{aligned}
2Se_2Cl_2 + 3H_2O &= H_2SeO_3 + 3Se + 4H^+ + 4Cl^- \\
2TeCl_2 + 2H_2O &= TeO_2 + 4H^+ + 4Cl^- \\
SeCl_4 + 3H_2O &= H_2SeO_3 + 4H^+ + 4Cl^-
\end{aligned}$$

The hydrolysis of S_2Cl_2 in the presence of considerable water is much more complicated, the resulting solutions containing eventually considerable precipitated and colloidal sulfur, moderate amounts of tri, tetra, and pentathionic acids, and small amounts of H_2SO_3, H_2SO_4, and H_2S, but no thiosulfate.

Physical properties of the halides

From the point of view of chemical equilibria, the sulfur-group halides have been incompletely studied. The fluorides have such great stability that dissociation equilibria would be extremely difficult to attain. Hydrolytic equilibria lie so far in favor of the products of hydrolysis that measurements are, for the most part, out of the question. In the case of the hexafluorides, spectroscopic and electron-diffraction data have made possible the calculation of entropies and free energies. The hexafluoride molecules are octahedral in shape, the S, Se, and Te atoms being at the center and the fluorine atoms at the corners of the octahedra. The highly electronegative character of fluorine suggests that bonds with it are to a considerable extent ionic in character; there must be enough covalent character, however, to maintain the well-defined bond directions, since it is known that in some trifluorides (PF_3, AsF_3) the molecular shape is pyramidal and does not correspond to the simple planar structure that would result if the fluoride ions were free to move about the atom to which they are attached.

As remarked above, all of the fluorides have a strong tendency to hydrolyze with water; the reaction is immeasurably slow with SF_6 and S_2F_{10}, and goes at a measurable rate with SeF_6 and TeF_6. S_2F_2 reacts rapidly with water, the products being S, SO_2, and HF [Trautz and Ehrmann, *J. prakt. Chem.*, **142,** 79 (1935)].

Of the chlorides, S_2Cl_2 and SCl_2 have been studied most. Both are of considerable importance in industry, especially in the manufacture of rubber. Chlorine reacts rapidly with sulfur to form the light-yellow, liquid monochloride, S_2Cl_2. The further reaction to form the dichloride,

SCl_2, is slow and requires several hours before equilibrium is reached. When the liquid dichloride is heated to 100° or higher, the equilibrium is displaced and the concentration of SCl_2 decreases. If this mixture is then cooled rapidly to 0° or room temperature, the recombination of S_2Cl_2 and Cl_2 proceeds slowly and in accord with the rate equation

$$-\frac{d(S_2Cl_2)}{dt} = k(S_2Cl_2), \text{ where } k = 0.0027 \text{ min}^{-1} \text{ at } 0^\circ$$

Different values of k are found when mixtures of S_2Cl_2 and Cl_2 that do not correspond to the composition SCl_2 are used. The reaction is quite complex, as is indicated by the fact that, for any given mixture of S_2Cl_2 and Cl_2, the rate of formation of SCl_2 is independent of the concentration of Cl_2.

The equilibrium constant of the slow, reversible reaction $S_2Cl_2 + Cl_2 = 2SCl_2$ is

$$K = \frac{(Cl_2)(S_2Cl_2)}{(SCl_2)^2} = 0.013$$

and is independent of the units used for expressing concentrations. The value 0.013 refers, presumably, to room temperature, 18°, but the investigators are not definite on this point [Spong, *J. Chem. Soc.*, 1547 (1933), 1283 (1934); Lowry and Jessop, *J. Chem. Soc.*, 323 (1931)]. There is some evidence for the existence of S_3Cl_4 in equilibrium with SCl_2 and S_2Cl_2,

$$SCl_2 + S_2Cl_2 = S_3Cl_4$$

A substance of this composition has been isolated at low temperatures; it decomposes extensively at room temperatures. The compound S_3Cl_2 is also thought to be present in S_2Cl_2 in small equilibrium amounts,

$$3S_2Cl_2 = S_3Cl_4 + S_3Cl_2$$

although it has never been isolated. In order to explain the boiling point of solutions of S_2Cl_2 in organic solvents, the existence of S_2Cl_4 has been postulated [Patrick and Hackerman, *J. Phys. Chem.*, **40**, 679 (1930)].

Recent experiments with radioactive sulfur dissolved in sulfur monochloride show that exchange of sulfur occurs, the rate being very slow at room temperature but conveniently measurable at 100°. It follows from this fact that sulfur monochloride always contains uncombined dissolved sulfur in equilibrium with it. Rate measurements on the exchange are best interpreted by assuming that the slow step in the exchange is the reaction

$$S_8 \text{ (in } S_2Cl_2) = S_6 \text{ (in } S_2Cl_2) + S_2 \text{ (in } S_2Cl_2)$$

The succeeding rapid reversible step is assumed to be $2S_2Cl_2 = S_2Cl_4 + S_2$ [Cooley and Yost, *J. Am. Chem. Soc.*, **62**, 2474 (1940)].

When S_2Cl_2 is distilled, b.p. = 138°, the residue becomes richer in sulfur, thus indicating decomposition. Vapor-density measurements indicate little if any decomposition in the gas phase at temperatures below 300°C. At higher temperatures, 300° to 800°, the decomposition becomes appreciable; the reaction expected is

$$S_2Cl_2 = S_2 + Cl_2$$

but the value of ΔH calculated from the equilibrium data is not in accord with that determined calorimetrically [Barton and Yost, *J. Am. Chem. Soc.*, **57**, 307 (1935)]. This fact indicates that the assumed reaction is accompanied by others. By utilizing molecular data and a

TABLE 80

THE PHYSICAL PROPERTIES OF THE SULFUR-GROUP FLUORIDES

	Melting Point (°C)	Boiling or Sublimation Point (°C)	Heat of Vaporization[a] (cal)	Heat of Formation (cal)	Atomic Distances (Å)	Frequencies of Vibration of Normal Modes[b] (cm^{-1})	Standard Molal Entropy, S°_{298} (cal/deg)
S_2F_2......	−120.5	−38.4		—			
SF_4.	−124.	−40.	5180	—			
SF_6 . .	−50.8	−63.8	5460	262,000	S—F, 1.58	775 645 525 363 617 965	69.6
S_2F_{10} .	(−53)	29	7000	(461,000)	S—S, 2.3 S—F, 1.58		
SeF_4. .	−13.5	93	—	—			
SeF_6.	−34.6	−46.6	6600	246,000	Se—F, 1.70	708 662 405 245 461 787	75.2
TeF_4....	—	—	—	—	—		
TeF_6....	−37.8	−38.9	6740	315,000	Te—F, 1.84	701 674 313 165 370 752	80.6
Te_2F_{10}...	(−14)	(60)	—	—	—		

[a] When the substance has a sublimation pressure of 1 atm. before it melts, the heat of vaporization refers to the change in state A(s) = A(g).

[b] The degeneracies of the frequencies for the hexafluorides are 1, 2, 3, 3, 3, 3, respectively, reading downward [Yost, *Proc. Ind. Acad. Sci.*, **8**, 333 (1938)].

reasonable value for the heat of formation of SCl_2, the data may be interpreted somewhat more satisfactorily on the basis of the reactions

$$\begin{aligned} S_2 + Cl_2 &= S_2Cl_2 \\ \tfrac{1}{2}S_2 + Cl_2 &= SCl_2 \\ 3S_2 &= S_6 \\ 4S_2 &= S_8 \end{aligned}$$

The value of ΔH calculated in this way agrees well with the thermal value (D. P. Stevenson, unpublished calculations). The equilibrium constants are expressed as a function of the temperature by the formulas,

$$\log_{10} \frac{P_{S_2Cl_2}}{P_{S_2}P_{Cl_2}} = \frac{7460}{T} - 5.33 (760°K < T < 1100°K)$$

$$\log_{10} \frac{P_{SCl_2}}{P_{S_2}^{1/2}P_{Cl_2}} = \frac{4478}{T} - 2.82 (760°K < T < 1100°K)$$

where pressures are expressed in atmospheres. However, the runs in which an excess pressure of chlorine was present give results that show a slight systematic deviation from those of the others, and it seems that for a complete treatment some further reaction that would depress even more the chlorine partial pressure must be considered. For this reason, and because some frequencies had to be guessed for SCl_2 and S_2Cl_2, the equilibrium constants given by the formulas are only approximations and are presented for lack of better values. The molar entropies at 298.1° are estimated to be 67.2 ± 1.0 cal/deg for $SCl_2(g)$ and 78.4 ± 2.5 cal/deg for $S_2Cl_2(g)$.

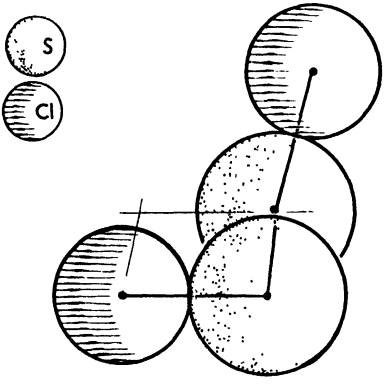

Fig. 60. The Molecular Structure of S_2Cl_2. Cl—S = 1.99Å; S—S = 2.05Å; ∠Cl—S—S = 103°.

Electron-diffraction experiments show the structure of S_2Cl_2 to be as shown in Fig. 60. The structure of SCl_2 is simply triangular, the Cl—S—Cl angle being 101° and the S—Cl distance being 1.99 Å. Whether in S_2Cl_2 there is free rotation about the S—S bond, or if the angle between Cl—S—S planes is 97°, has not been determined definitely; if there is no free rotation, the 97° structure is correct and not a cis (0°) or trans (180°) structure [Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938)].

Selenium monochloride, Se_2Cl_2, decomposes quite extensively when distilled, b.p. > 125°, and in such a way that a residue of selenium remains if the distillation is continued until no further chloride comes over. Vapor-density measurements must be carried out at the temperature of boiling selenium or above, and at such temperatures decomposition is extensive. There is some evidence for believing that the vapors from Se_2Cl_2 consist of $SeCl_2$.

When placed in contact with water, Se_2Cl_2 hydrolyzes slowly to give solid selenium and H_2SeO_3 and HCl in solution. The reaction is reversible, for selenium in contact with a strong hydrochloric acid solution of H_2SeO_3 is slowly converted to the dark-red liquid monochloride. Se_2Cl_2 is a good solvent for Se (9.73 parts Se in 100 parts Se_2Cl_2 at 25°), S (48.81 parts in 100 at 25°), and iodine. It does not react with SO_2, but does react reversibly with SeO_2 to form $SeOCl_2$ and Se [Lehner and Kao, *J. Am. Chem. Soc.*, **48**, 1550 (1926)]. The molecular structure of Se_2Cl_2 is doubtless much like that of S_2Cl_2.

The tetrachloride of selenium, $SeCl_4$, does not exist as such in the vapor phase but is dissociated completely into $SeCl_2$ and Cl_2. This conclusion is based on the experimental facts that the vapor density of $SeCl_4$ is just one-half the formula weight, and that the vapor pressure of $SeCl_4(s)$ is depressed by the presence of excess chlorine. The following results show the second effect [Yost and Kircher, *J. Am. Chem. Soc.*, **52**, 4680 (1930)].

Vapor Pressure of Pure $SeCl_4(s)$

Temperature (°C)	p (mm)	Temperature (°C)	p (mm)
109	11.3	161	203
131	42.6	171	318
150	117.4	180.5	482

Vapor Pressure of $SeCl_4(s)$ in Presence of Excess Chlorine

Temperature (°C)	Pres. Excess Chlorine, p_e (mm)	Pres. $SeCl_4$, p (mm)	Vapor Pressure of Pure $SeCl_4$ (mm)
146	346	20	96
161	358	56	203
171	366	123	318
176	370	179	397

$SeCl_2$ does not appear to exist in the liquid or solid state, mixtures of that composition consisting of Se_2Cl_2 and $SeCl_4$.

The bromides of S, Se, and Te resemble in many respects the chlorides, but, as is to be expected, are not as stable as the chlorides. S_2Br_2 and Se_2Br_2 have not been studied as extensively as the corresponding chlorides.

SBr_4 does not exist at room temperatures; $SeBr_4$, like $SeCl_4$, decomposes, on heating, to $SeBr_2$(g) and Br_2.

The iodides of sulfur and selenium do not exist under ordinary conditions. When a carbon tetrachloride solution of iodine is shaken with solid selenium until equilibrium is attained, the solution contains the monoiodide, Se_2I_2, in amounts, at 25°, given by the equilibrium relation $K = (Se_2I_2)/(I_2) = 0.0127$. If the solvent is ethylene bromide, both Se_2I_2 and SeI_4 are found; at 25°, $(Se_2I_2)/(I_2) = 0.0208$, and $(SeI_4)/(I_2)^2 = 0.0409$, the concentrations being expressed as mole fractions [McCullough and Beckman, Thesis, Calif. Inst. Tech., 1936]. The fact that iodine does not react with solid S or Se is of importance in measurements of the following equilibria [Pollitzer, *Z. anorg. Chem.*, **64**, 121 (1909); Rolla, *Gazz. Chim.*, **42**, II, 432 (1912)]:

TABLE 81
THE PHYSICAL PROPERTIES OF THE SULFUR-GROUP HALIDES

	Melting Point (°C)	Boiling Point[a] (°C)	Heat of Formation (cal)
S_2Cl_2	−80	138	14,300
S_2Br_2	−46	90 dec.	4,000
SCl_2	−78	59 dec.	12,000
SCl_4	−31	dec.	13,700
Se_2Cl_2	−85	127 dec.	22,130
$SeBr_2$ (g)		227 dec	
$SeCl_2$ (g)			10,000
$SeBr_2$			
$SeCl_4$		191 subl.	46,120
$SeBr_4$	dec		
$TeCl_2$[b]	175	324	
$TeBr_2$[c]	280	339	
TeI_2			
$TeCl_4$[d]	214	414	77,100
$TeBr_4$	380	421	49,300

[a] The boiling points are the temperatures at which the total vapor pressure is 760 mm; in most cases the vapor consists of decomposition products along with the original substance. Thus $TeBr_4$ is about 90 % decomposed at 421° into $TeBr_2$ and Br_2; $SeCl_4$ is completely decomposed at 191° into $SeCl_2$ and Cl_2; SCl_2 vapor consists principally of S_2Cl_2 and Cl_2. $TeCl_2$ and $TeBr_2$ are not appreciably decomposed at their B.P.

[b] $TeCl_2$ in the vapor phase is probably a nonlinear molecule with Te—Cl = 2.36 Å.

[c] $TeBr_2$ in the vapor phase is nonlinear with < Br—Te—Br = 98° and Te—Br = 2.51 Å (R. A Spurr, unpublished experiments).

[d] $TeCl_4$ [Stevenson and Shomaker, *J. Am. Chem. Soc.*, **62**, 1267 (1940)] is not a regular tetrahedral molecule).

$$S(s, r) + 2HI(g) = I_2(s) + H_2S(g), \qquad \Delta F^\circ_{298} = -8470 \text{ cal}$$
$$Se(s, h) + 2HI(g) = I_2(s) + H_2Se(g), \qquad K_{300} \text{ (atm)} = 0.055$$

Aside from the melting and boiling points and the fact that the vapors decompose at higher temperatures, little is known about the di- and tetrahalides of tellurium. Noteworthy is the fact that $TeCl_2$ and $TeCl_4$ when molten are good conductors of electricity, their specific conductivities being, respectively, 0.0402 (at 206°) and 0.1145 (at 236°) [Biltz and Voight, *Z. anorg. Chem.*, **133**, 297 (1924)]. The value for molten $TeCl_4$ is approximately that of a 1 n solution of KCl. This high conductivity of $TeCl_2$ and $TeCl_4$ is an indication of a salt-like character, and there can be no doubt that these substances in the liquid state are rather highly ionized. The nature of the ions has not been established, but they are probably Cl^-, Te^{++}, Te^{++++}, $TeCl^+$, and $TeCl_2^{++}$.

The Oxyhalides of Sulfur, Selenium, and Tellurium

Preparation

The oxyfluorides are prepared by rather special methods. Thionyl fluoride, SOF_2, results when $SOCl_2$ (liquid) and AsF_3 (liquid) are mixed and gently warmed. The reaction goes at a moderate rate, the products being SOF_2, SO_2, and SOClF, and rather careful fractionation at low temperatures is necessary to obtain pure thionyl fluoride. The rather inert gas sulfuryl fluoride, SO_2F_2, is best prepared by the thermal decomposition of dry calcium or barium fluosulfonate, $Ba(SO_3F)_2$, at red heat [Traube, Hoerenz, and Wunderlich, *Ber.*, **52**, 1272 (1919); Trautz and Ehrman, *J. prakt. Chem.*, **142**, 79 (1935)].

$$Ba(SO_3F)_2 = BaSO_4 + SO_2F_2$$

Sulfuryl chlorofluoride, SO_2ClF, is prepared by heating a mixture of SO_2Cl_2 (365 g), SbF_3 (187 g), and $SbCl_5$ (40 cc) to 300° in a closed vessel. The final pressure of the reacting mixture becomes over 100 pounds per square inch, but the product is bled off at around 90 pounds pressure. Fractional distillation is necessary to separate the SO_2ClF from the gaseous reaction products [Booth and Herrmann, *J. Am. Chem. Soc.*, **58**, 63 (1936)]. The compound hydrolyzes rapidly in water, it has a pungent odor but does not fume in air, and it does not attack dry glass, mercury, or brass.

Thionyl chloride, $SOCl_2$, can be prepared by passing SO_2 over PCl_5.

$$SO_2 + PCl_5 = SOCl_2 + POCl_3$$

Both $SOCl_2$ (b.p. 78°) and $POCl_3$ (b.p. 107°) are liquids at ordinary temperatures, and the mixture of the two must be fractionally distilled in order to recover the thionyl chloride. Inasmuch as thionyl chloride finds application in organic preparations, its manufacture by a more convenient process is desirable. One process consists in passing chlorine into a mixture of SO_3 and S_2Cl_2 heated to 75–80°.

$$SO_3 + S_2Cl_2 = SOCl_2 + S + SO_2$$
$$2S + Cl_2 = S_2Cl_2$$

Other processes consist in treating PCl_3 with SO_2Cl_2,

$$SO_2Cl_2 + PCl_3 = POCl_3 + SOCl_2$$

and in passing sulfur dioxide and phosgene, $COCl_2$, over charcoal heated to 200° or above; the $COCl_2$ may be replaced by a mixture of CO and Cl_2. Of chemical but not practical interest is the reaction between sulfur and Cl_2O, the latter combining as a whole with sulfur according to the equation

$$S + Cl_2O = SOCl_2$$

With solid sulfur the reaction is rather violent; it proceeds smoothly and efficiently if the chlorine monoxide is passed into S_2Cl_2 containing dissolved sulfur and cooled to −12°.

Sulfur oxybromide or thionyl bromide, $SOBr_2$, is prepared by treating $SOCl_2$ with dry HBr (g) at 0°, followed by fractional distillation *in vacuo.* [Booth, *Inorganic Syntheses,* McGraw-Hill, New York, 1939, pp. 113 and 151]. It is a yellowish-orange liquid that is rather unstable and that decomposes somewhat into S_2Br_2, SO_2, and Br_2 at room temperature (slow reaction) and much more so (30%) when it is distilled at its normal boiling point of 137° [Mayes and Partington, *J. Chem. Soc.,* 2594 (1926)].

Sulfuryl chloride, SO_2Cl_2 (b.p. 69°), is readily prepared by dissolving camphor in liquid SO_2 and then passing chlorine through the solution. Camphor, at 0°, is capable of dissolving some 300 volumes of SO_2 to form a clear liquid; and when chlorine is passed through this liquid, SO_2Cl_2 is formed and can be distilled from the mixture with little difficulty. The combination also takes place readily in the presence of activated charcoal or silica, if the reaction tube is kept cool and is so shaped that liquid SO_2Cl_2 is always present.

$$SO_2 + Cl_2 = SO_2Cl_2$$

Chlorine and sulfur dioxide in the absence of light or a catalyst react only slowly at room temperature; the rate increases with temperature, but the reverse reaction of decomposition soon predominates, and little or no SO_2Cl_2 is obtained at 200° and higher. Animal charcoal acts as a catalyst, but even in its presence the combination of gaseous SO_2 and Cl_2 is slow at 110–180° [Trautz, *Z. Electrochem.,* **14,** 534 (1908)]. The rate of the reaction is greatly increased by irradiation of the gaseous mixture with light that is absorbed by chlorine. The instability of SO_2Cl_2 indicates that the corresponding bromide would be still more unstable; sulfuryl bromide is not known.

When SO_3 is dissolved in cold sulfur monochloride, or if chlorsulfonic acid, HSO_3Cl, is treated with P_2O_5, the pyrosulfuryl chloride, $S_2O_5Cl_2$ (b.p. 145°), is formed. It is the anhydride of chlorsulfonic acid.

All of the known oxyhalides of sulfur, with the exception of $SOBr_2$, are colorless.

Selenium oxyfluoride is formed when dry silver fluoride is treated with $SeOCl_2$. This method of preparation is a general one often used to prepare fluorides from chlorides or bromides. Besides AgF (dry), HgF_2 is used in some cases with considerable success [Henne, *J. Am. Chem. Soc.*, **60,** 1569 (1938)]. $SeOF_2$ is a colorless, fuming liquid with a characteristic odor; it hydrolyzes rapidly with water to form H_2SeO_3 and HF [Prideaux and Cox, *J. Chem. Soc.*, **738,** (1928)].

Selenium oxychloride, $SeOCl_2$, a well-defined compound, is easily prepared by treating a suspension of $SeCl_4$ in carbon tetrachloride with SeO_2; the $SeOCl_2$ formed is soluble in carbon tetrachloride and is freed from that solvent by evaporation [Lehner, *J. Am. Chem. Soc.*, **42,** 2498 (1920)].

$$SeCl_4 + SeO_2 = 2SeOCl_2$$

Selenium oxychloride, when pure, is an almost colorless liquid miscible in all proportions with CCl_4, $CHCl_3$, CS_2, and benzol. It is formed in the reversible reaction

$$2Se_2Cl_2 + SeO_2 = 2SeOCl_2 + 3Se$$

and by the action of HCl(g) on a mixture of SeO_2 and a dehydrating agent

$$\begin{aligned} SeO_2(g) + 2HCl(g) &= SeO_2{\cdot}2HCl(l) \\ SeO_2{\cdot}2HCl &= SeOCl_2 + H_2O \end{aligned}$$

The oxybromide is prepared by warming mixtures of SeO_2 and $SeBr_4$; it is a yellow crystalline solid. Compounds of the formula SeO_2Cl_2 and SeO_2Br_2 are not known.

Tellurium does not form oxyhalides of the distinctive character observed with sulfur and selenium. The partial hydrolysis of TeF_4, $TeCl_4$, and $TeBr_4$ leads to compounds containing oxygen and the halogen, but their preparation free from water is not easy nor does it lead to substances of great interest.

Physical and chemical properties of the oxyhalides

The ordinary physical properties of the oxyhalides are shown in Table 82. They are characterized by being liquids (except $SeOBr_2$) and, accordingly, more or less volatile.

The compounds $SOCl_2$ and $SeOCl_2$ may be looked upon as derivatives of the dioxides. They hydrolyze more or less readily and completely with water in accordance with the reaction

$$YOX_2 + 2H_2O = H_2YO_3 + 2HX$$

where Y stands for S or Se and X for the halogens. The rate of hydrolysis is most rapid with SOF_2 and $SeOF_2$ and least with $SOCl_2$ and $SeOCl_2$. When the vapors are strongly heated, they decompose into a mixture of the monochloride, dioxide, and halogen, a higher temperature being required to decompose the fluorides than the chlorides and bromides; the sulfur compounds require a higher temperature for decomposition than do those of selenium.

Thionyl chloride reacts with a number of substances. With hot lead formate and oxalate, it is reduced to S_2Cl_2 [Schumb, *J. Am. Chem. Soc.*, **57,** 260 (1935)]. It may act as a chlorinating agent or a simple oxidizing agent, or, in the case of organic compounds, it can serve to introduce chlorine or —SO groups. Owing to its moderately high dielectric constant, 9.05 at 22°, it is a moderately good ionizing solvent.

Selenyl chloride has a high dielectric constant, a specific conductance of 2×10^5 mhos, and shows interesting properties as an ionizing solvent [Smith, *Chem. Rev.*, **23,** 165 (1938)]. Its action on other substances is one of chlorination or oxidation. It is a good solvent for S, Se, Te, Br_2, and I_2, the solvent action being accompanied, in the case of Te, and possibly also in the case of S, by reaction to form $TeCl_4$ and S_2Cl_2. When mixed with sulfur trioxide, selenyl chloride forms a thick, heavy solution with the property of dissolving such resistant substances as Al_2O_3, Cr_2O_3, and oxides of the rare earths.

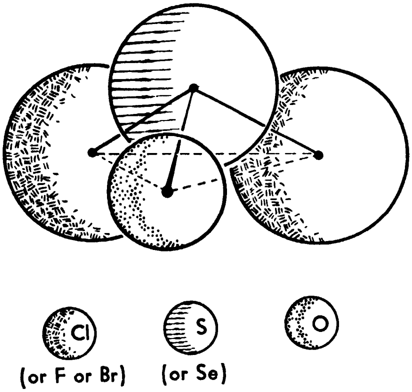

Fig. 61. The Molecular Structures of $SOCl_2$, SOF_2, $SOBr_2$, **and** $SeOCl_2$.

	A—O	A—X	∠X—A—A	∠X—A—O
$SOCl_2$.	1.45Å	2.05Å	97.5°	107.5°
SOF_2 .	1.45	1.6	106(?)	114(?)
$SOBr_2$.	1.45	2.27	96	108
$SeOCl_2$	1.61	1.7	106(?)	114(?)

The structures of SOF_2, $SOCl_2$, $SOBr_2$, and $SeOCl_2$ have been determined by the electron-diffraction method. As one might expect, the configurations are similar: they are pyramidal and differ only in the interatomic distances and bond angles, as indicated in Fig. 61 [Stevenson and Cooley, *J. Am. Chem. Soc.*, **62,** 2477 (1940); Palmer, *J. Am. Chem. Soc.*, **60,** 2360 (1938); Stevenson and Beach, unpublished experiments]. The pyramidal structure is characteristic of these molecules; if the bonding were purely ionic, a planar structure would be expected; accordingly, the bonding must be considered to be, in part at least, covalent.

TABLE 82

THE PHYSICAL PROPERTIES OF THE SULFUR-GROUP OXYHALIDES

	Melting Point (°C)	Boiling Point (°C)	Density of Liquid	Heat of Vaporization (cal)	Heat of Formation (cal)
SOF_2	−110	−30	3.0		
$SOCl_2$	−104.5	78.8	1.656 (14.5°)	7,480	50,200
$SOBr_2$	−50	137	2.67 (25°)	10,400	
SO_2F_2*	−136.7	−55.4	—	4,790	—
SO_2ClF	−124.7	7.1	1.623 (0°)	6,340	—
SO_2Cl_2	−54.1	69.1	1.667 (20°)	6,700	92,900
$S_2O_5Cl_2$	−37.5	153	1.837	13,200	166,500
$SeOF_2$	4.6	124	2.67	—	—
$SeOCl_2$	8.5	176.4	2.424 (22°)	—	—
$SeOBr_2$	41.7	—	3.38 (50°)	—	—

Dielectric Constants

$SeOCl_2$	20°	46.2
	10°	51.00
$SOCl_2$	22°	9.05

Entropies

	S°_{298} (cal/deg/mole)
$SOCl_2(g)$	73.55
$SO_2Cl_2(g)$	74.34

* The values for SO_2F_2 were recently determined by H. Russell, Jr. (unpublished). For the vapor pressures, $\log_{10} p_{mm} = 23.38463 - \frac{1584.12}{T} - 5.65871 \log_{10} T$.

The Raman spectrum of $SeOCl_2$ is not known. The spectra of SOF_2 and $SOCl_2$ are given here for purposes of comparison to show the effect of replacing chlorine by fluorine; the fact that the S—F bond is stronger than the S—Cl bond, and the additional fact that fluorine is lighter than chlorine, lead to higher frequencies for SOF_2 than for $SOCl_2$ for those modes of vibration in which the S—F and S—Cl bonds undergo appreciable changes in length or orientation [Yost, *Proc. Ind. Acad. Sci.*, **8**, 333 (1938)].

TABLE 83

RAMAN FREQUENCIES OF $SOCl_2$ AND SOF_2

$SOCl_2$	192	282	343	443	488	1229	cm^{-1}
SOF_2	326	395	529	720	795	1312	cm^{-1}

Sulfuryl fluoride, SO_2F_2, resembles the hexafluoride, SF_6, in inertness. SO_2F_2 is not decomposed appreciably in iron vessels at incipient red heat;

it does not hydrolyze rapidly in water. In warm dilute alkali (about 0.5 n), it hydrolyzes rapidly, almost quantitatively, according to the equation,

$$SO_2F_2 + 2OH^- = SO_3F^- + F^- + H_2O$$

The fluosulfonate ion is further hydrolyzed to sulfate and fluoride ions on heating in strongly acid or alkaline solutions (see Chapter 10, p. 347). It will react with ammonia to form sulfamide, $SO_2(NH_2)_2$ [Traube and Reubke, *Ber.*, **56,** 1662 (1923)].

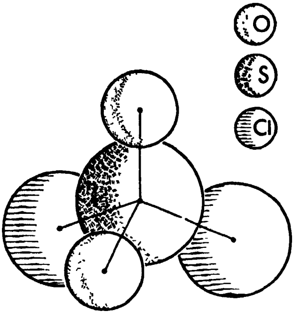

Fig. 62. The Molecular Structure of SO_2Cl_2. S—O = 1.43 Å; S—Cl = 1.99 Å; ∠O—S—O = 120°; ∠Cl—S—Cl = 111°; ∠Cl—S—O = 106.5°.

Sulfuryl chloride, SO_2Cl_2, hydrolyzes readily in water to form sulfuric and hydrochloric acids, and for this reason it was once employed as a component in smoke-producing mixtures; it is less satisfactory for this purpose, however, than a number of other compounds, for example, HSO_3Cl, $HSO_3Cl + SO_3$, SO_3, and $TiCl_4$, and in this application it no longer finds use. Bottles of sulfuryl chloride, if not kept tightly stoppered, absorb moisture slowly from the air to form H_2SO_4 and HCl. The compound may be looked upon as a derivative of SO_3 in which one oxygen atom has been replaced by two chlorine atoms.

When heated to 280° or above, gaseous sulfuryl chloride decomposes at a measurable rate into SO_2 and chlorine,

$$SO_2Cl_2 = SO_2 + Cl_2$$

Measurements of the rate indicate that while the decomposition may be partly homogeneous, it is strongly affected by catalysts. The sulfuryl chloride prepared through the use of camphor decomposes more rapidly, at the same temperature, than does that prepared with a silica catalyst [Ramsperger, unpublished results, 1930. See Kassel, *Kinetics of Homogeneous Gas Reactions*, p. 235].

Inasmuch as sulfuryl chloride decomposes completely into SO_2 and Cl_2 at around 300°, and since SO_2 and Cl_2 can be caused to combine at room temperature, equilibrium will be attained at intermediate temperatures with all three compounds present in measurable amounts. Trautz found that the rate of attainment of equilibrium is immeasurably slow in the temperature range 100–200°; however, with animal charcoal as a catalyst, equilibrium is reached in a reasonable time [Trautz, *Z. Electrochem.*, **14,** 534 (1908)]. The measurements of Trautz and of others [Landolt Börnstein, *Tabellen,* 3rd Erg Bd., Vol. 3, p. 2605 (1936); 1st Erg. Bd., Vol. 2, p. 1418 (1923)] are not altogether satisfactory, since there is some indication that equilibrium was not reached. This is apparent in the following table, which contains results calculated by Dr. D. P. Stevenson from equilibrium and molecular data. Energy values are expressed in kilocalories per mole. The drift in ΔH_0° indicates a lack of consistency between equilibrium and molecular data. An approximate value of ΔH° for the reaction is 12,900 cal; calorimetric measurements lead to $\Delta H^\circ = 14{,}400$ cal. It would be of interest to find a catalyst so that more careful measurements could be made in the range 25–100°; bromine or iodine might act catalytically, since it is not uncommon to find that BrCl and ICl are more reactive than chlorine alone. Equilibrium is established more readily in the presence of anhydrous aluminum chloride owing to the formation of the intermediate $AlCl_3{\cdot}SO_2$. A film of sulfuric acid on the walls of a glass reaction vessel has been found to act catalytically in the combination reaction.

TABLE 84
EQUILIBRIUM CONSTANTS FOR THE REACTION
$SO_2Cl_2(g) = SO_2(g) + Cl_2(g)$

$$K_{atm} = \frac{P_{SO_2}P_{Cl_2}}{P_{SO_2Cl_2}}$$

Temp. (°K)	K_{atm}	$\frac{\Delta F^\circ}{T}$	ΔH_0°
303	0.0288	7.05	12.8
313	.0506	5 93	12.9
323	.0837	4.93	13.1
375	2.37	−1.71	12.8
432	8.9	−4.34	13.7
464	13 1	−5.10	14.4

Sulfuryl chloride acts as an oxidizing and chlorinating agent as well as a substance useful for introducing the —SO_2 group into other compounds. When it is mixed with ammonia in benzol solution, sulfimide, $(SO_2NH)_3$, is formed together with several other chain-like compounds.

CHAPTER 10

The Oxides and Oxyacids of Sulfur, Selenium, and Tellurium

The Oxides of Sulfur, Selenium, and Tellurium

Formation and properties of the monoxides

When sulfur, selenium, or tellurium is heated in oxygen, the dioxide is formed. With excess oxygen and a catalyst, SO_2 combines with more oxygen to form SO_3, but SeO_3 and TeO_3 are not formed in this way to any appreciable extent. It is possible, by special methods, to obtain the monoxides of sulfur and tellurium. Elementary tellurium dissolves in liquid sulfur trioxide to form a red mixture which decomposes when heated to give vapors of SO_3 and a residue of $TeSO_3$ (softening point, 30°); this residue decomposes further to give sulfur dioxide and a black solid which appears to be TeO, an oxide corresponding to the well-known dihalides.

When a mixture of SO_2 and sulfur vapor is passed at from 1 to 10 mm pressure through an electric discharge (3,000–20,000 volts), sulfur monoxide, SO, is formed. This substance is known only in the gas phase, and in this state it can be kept without extensive decomposition for several days. When the gas is condensed at liquid-air temperatures to a solid (orange red) and the latter allowed to melt, decomposition into sulfur dioxide and sulfur takes place completely and rapidly. If an alkali solution is poured onto the solid, the resulting mixture at room temperature is found to contain hyposulfite, $S_2O_4^=$. Sulfur monoxide is not the anhydride of hyposulfurous acid, $H_2S_2O_4$; its hydrolysis must yield both sulfur and hyposulfite.

$$3SO + H_2O = H_2S_2O_4 + S$$

Gaseous sulfur monoxide does not react with oxygen at room temperatures. Sulfur monoxide can be formed also in a purely chemical way by heating thionyl chloride (and $SOBr_2$) with Na (100°), Ag (150°), Sn (200°), Mg (400°), or Al (450°).

The detection of sulfur monoxide depends on characteristic absorption bands extending from 3130 Å to shorter wave lengths. The emission spectrum was known before the gas was prepared in workable quantities.

The preparation and properties of SO are due to Schenk. [See Schenk, *Z. anorg. Chem.*, **233,** 385 (1937) *et ante.*] The gas is presumably paramagnetic, since the ground state of the molecule is $^3\Sigma$. The energy levels, both rotational and vibrational, are given in cm^{-1} by the empirical formula

$$\frac{\epsilon}{hc} = (.70894 - .00562(v + \tfrac{1}{2}))J(J + 1) + 1123.73(v + \tfrac{1}{2}) - 6.116(v + \tfrac{1}{2})^2$$

This information, together with the spectroscopic data for S_2 and O_2 (Herzberg, *Molecular Spectra*), has been used to calculate equilibrium constants for the reactions

$$\tfrac{1}{2}S_2(g) + \tfrac{1}{2}O_2(g) = SO(g)$$
$$\tfrac{1}{2}S_2(g) + SO_2 = 2SO(g)$$

A few representative values of $\log_{10} K$ are given in the following table [unpublished calculations by D. V. R. Golding]. The older calculations by Montgomery and Kassel [*J. Chem. Phys.*, **2,** 417 (1934)] were based on incorrect values for the dissociation energies of S_2 and SO.

Table 85

EQUILIBRIUM CONSTANTS FOR THE REACTIONS

$$\tfrac{1}{2}S_2(g) + \tfrac{1}{2}O_2(g) = SO(g)$$
$$\tfrac{1}{2}S_2(g) + SO_2(g) = 2SO(g)$$

T (°K)	Pressures in Atmospheres	
	$\log_{10} K_1$ $\left[K_1 = \frac{(SO)}{(S_2)^{1/2}(O_2)^{1/2}}\right]$	$\log_{10} K_2$ $\left[K_2 = \frac{(SO)^2}{(S_2)^{1/2}(SO_2)}\right]$
298.1	−5.45	−71.52
500	−3.14	−40.32
1000	−1.43	−17.98
1500	− .86	−10.54
2000	− .58	− 6.84

	S_2	O_2	SO
D_0 (e.v.)*	3.6	5.082	4.002

$$SO_2(g) = \tfrac{1}{2}S_2(g) + O_2(g)$$
$$\Delta E_0^\circ = 3.725 \text{ e.v.}$$

---

* Dissociation energy in electron volts per molecule.

From the results shown in the last column, it is evident that only a very small equilibrium concentration of SO can be attained in a gaseous mixture of S_2 and SO_2 even at 2000°. The fact that SO is produced from

S_2 and SO_2 in an electrical discharge must depend on the presence of activated molecules having greater energies than are possible in the equilibrium mixture obtaining at 2000°K.

Preparation of dioxides

The dioxides of sulfur, selenium, and tellurium may be prepared simply by heating the elements with oxygen. Sulfur burns readily in air, with the formation of the dioxide and small amounts (up to 3.6%) of SO_3; large amounts of the dioxide are formed in the process of roasting sulfide ores in the presence of air.

$$MS + \tfrac{3}{2}O_2 = MO + SO_2$$

Sulfur dioxide can be easily prepared in small quantities for experimental purposes by treating sulfites or bisulfites with sulfuric, hydrochloric, or other strong acids. In the liquid form, it is now furnished at low cost in steel cylinders.

The preparation of selenium dioxide by the direct combination of selenium and oxygen is not always the most convenient method for obtaining the substance. The rate of oxidation by oxygen is more rapid if the oxygen is first passed through fuming nitric acid before passing it rapidly over molten selenium [Jul. Meyer, *Ber.*, **55**, 2082 (1922)]. In the more common method of preparation, black selenium of commerce is treated with nitric acid (6 n or stronger); upon heating the mixture, red fumes of nitrogen dioxide are given off and the selenium dissolves as H_2SeO_3. The solution is evaporated to dryness, and the resulting white solid, which is first H_2SeO_3 and on further heating SeO_2, is used as such or is purified by sublimation.

Tellurium dioxide is also best prepared by treating elementary tellurium with 6 n nitric acid. The resulting solution may be evaporated to dryness and the white residue, $2TeO_2{\cdot}HNO_3$, then ignited, or, if the acid solution is neutralized, the white, solid TeO_2 will precipitate out. To obtain a very pure product, it is best to recrystallize the basic nitrate, $2TeO_2{\cdot}HNO_3$, from 6 n HNO_3. In this operation the nitric acid solvent is heated to 70° so that as much as possible of the basic nitrate dissolves; the solution is then either cooled and the basic nitrate allowed to precipitate out, or the acid solution is evaporated at 80°. If the solution is heated too strongly, the basic nitrate decomposes into the dioxide. This method of purification is an effective one for obtaining tellurium free from the common impurity, copper. If selenium is also present, the tellurium dioxide is dissolved in 10 n hydrochloric acid and the resulting solution saturated with sulfur dioxide and heated to boiling when all of the selenium and a small amount of tellurium is precipitated. This mixture is filtered and the filtrate diluted to five times its original volume and again saturated with sulfur dioxide. The grey precipitate that comes down consists of metallic tellurium, and it may be converted to the dioxide by the nitric acid treatment already described above [Schuhmann, *J. Am. Chem. Soc.*, **47**, 356 (1925); Norris, Fay, and Edgerly, *Am. Chem. J.*, **23**, 107 (1900)]. Tellurium dioxide also results when tellurium or the tellurides are burned in air or oxygen; the flame has a bluish color.

Trioxides

The trioxides of sulfur, selenium, and tellurium have all been prepared, but the preparation of the two latter presents difficulties.

Sulfur trioxide is formed in the first step of the contact process for the manufacture of sulfuric acid in which sulfur dioxide and oxygen are heated together in the presence of a catalyst. The reaction is immeasurably slow at room temperature; at temperatures at which the uncatalyzed reaction is at all rapid, the equilibrium is so far displaced toward the $SO_2 + O_2$ side that the yield of the trioxide is very small. The rate of the reaction is greatly increased if the mixture of sulfur dioxide and air is led over finely divided or spongy platinum (best), nickel and cobalt sulfates, or the oxides of vanadium, tungsten, molybdenum, chromium, or iron. The optimum temperature with respect to rate of reaction and yield is around 665°; in some cases the gases are passed over the catalyst at this temperature and then over the same catalyst at 450–500°, the yield being thereby increased. Small amounts of arsenic "poison" the catalysts, and they then become ineffective. Arsenic occurs in many sulfides, and when roast gases are used as a source of sulfur dioxide, the difficulties with the contact process may be considerable if the arsenious oxide formed is not removed. Too much and too little moisture in the reaction mixture decreases the yield of the trioxide; if the SO_2-air mixture is first passed through concentrated sulfuric acid, the optimum moisture content is attained.

The reaction leading to the formation of sulfur trioxide has been thoroughly studied by several groups of investigators, and their results agree remarkably well [Bodenstein and Pohl, *Z. Electrochem.*, **11**, 373 (1905); Taylor and Lehner, *Z. phys. Chem.*, *Bodenstein Festb.*, 30 (1931); and Kapustinsky and Shamovsky, *Acta Physchim.*, *U.S.S.R.*, **4**, 791 (1936)]. This agreement is shown by combining the $(F^\circ - H_0^\circ)/T$ functions for SO_3, SO_2, and O_2, calculated from molecular data, with the experimental $\Delta F^\circ/T$ values, and noting the constancy of the values of ΔH_0°. The consistency is unusually good, as may be seen in the following table (D. P. Stevenson, unpublished calculations). The free-energy equation given by Lewis and Randall [*Thermodynamics*]

$$SO_2(g) + \tfrac{1}{2}O_2(g) = SO_3(g)$$
$$\Delta F^\circ = -22{,}600 + 21.36T$$

agrees closely with the more recent values given in the table. Below 400°C sulfur trioxide is seen to be only slightly decomposed, but above 900°C the decomposition is extensive.

Table 86

ΔF° AND ΔH_0° FOR THE REACTION $SO_2 + \frac{1}{2}O_2 = SO_3$

Ref.	T (°K)	$\log_e K_{atm}$	$\frac{\Delta F^\circ}{T}$ (cal/mole)	$-\Delta H_0^\circ$ (kcal/mole)
B & P	801	3.442	−6.84	22.85
	852	2.625	−5.21	22.95
	900	1.880	−3.73	22.95
	953	1.173	−2.33	22.95
	1000	0.616	−1.22	23.02
	1062	−0.046	0.09	23.05
	1105	−0.465	0.93	23.10
	1170	−1.028	2.04	23.20
				Ave. 23.01 ± 0.08
T & L	933	1.451	−2.88	23.00
	936	1.386	−2.75	22.95
	943	1.274	−2.53	22.92
	945	1.249	−2.48	22.93
	945	1.274	−2.53	22.97
				Ave. 22.95 ± 0.02
K & S	850	2.567	−5.10	22.80
	852	2.502	−4.96	22.75
	876	2.311	−4.59	23.05
	876	2.240	−4.45	22.95
	902	1.882	−3.74	23.00
	919	1.528	−3.03	22.80
	941	1.378	−2.72	23.05
	954	1.212	−2.41	23.05
	965	0.981	−1.95	22.90
	1001	0.625	−1.24	23.06
	1001	0.643	−1.28	23.10
				Ave. 22.96 ± 0.10

$\Delta H_0^\circ = -22{,}970$ cal/mole

t (°C)	ΔF° (cal/mole)	K_{atm}
25	−16,960	2.57×10^{12}
526.9	− 5,630	3.45×10
926.9	+ 3,290	2.50×10^{-1}

The problems attending the formation of SO_3 from SO_2 and O_2 are of historical interest in that progress in its manufacture followed closely the advances in chemical thermodynamics. Furthermore, sulfur trioxide is necessary in the convenient preparation of strong sulfuric acid (oleum), and this substance made possible many rapid and remarkable developments in synthetic organic chemistry; advances in theories of molecular structure were greatly influenced by the variety of organic compounds that chemists found it possible to prepare. Perhaps no other substances have influenced pure science and industry as much as have sulfur trioxide and sulfuric acid.

Sulfur trioxide can be prepared by heating anhydrous ferric sulfate, $Fe_2(SO_4)_3$, to some 600–700°, and this process was at one time its principal source. The following table shows the total equilibrium pressure, p, in millimeters of SO_3, SO_2, and O_2 above $Fe_2(SO_4)_3$-Fe_2O_3 at a few temperatures; the fraction of the total pressure due to SO_3 is a function of the temperature and may be calculated from the free-energy equation given above. The dry distillation of other sulfates has been suggested for the same purpose, but, with the exception of sodium pyrosulfate and a few others of little practical importance, the decomposition temperatures are so high that SO_2 and O_2 rather than SO_3 results. When convenient to do so, SO_3 may be prepared readily and pure by allowing SO_2 and ozone, O_3, to come together at room temperature. Still another reaction that produces SO_3 is that between NO and SO_2 at high pressures, 500 atm, of NO and at room temperatures. The rate is said to be conveniently rapid [Briner and Wroczynski, *J. chim. phys.*, **9**, 105 (1911)]. The reaction is

TABLE 87

DISSOCIATION PRESSURES OF $Fe_2(SO_4)_3$

$Fe_2(SO_4)_3(s) = Fe_2O_3(s) + 3SO_3(g)$; $SO_3(g) = SO_2(g) + \frac{1}{2}O_2(g)$

Temperature (°C)	p (mm)	Temperature (°C)	p (mm)
550	6	700	445
600	26	721	750
650	107		

$p = p_{SO_3} + p_{SO_2} + p_{O_2}$

$$NO + SO_2 = SO_3 + \tfrac{1}{2}N_2$$

Nitrogen dioxide in the absence of moisture does not react readily with sulfur dioxide at room temperatures; and even when heated, the reaction yields, in addition to sulfur trioxide, other sulfur-containing compounds. In a moist atmosphere, nitrosyl bisulfate, $NOHSO_4$, and sulfuric acid are formed from mixtures of the dioxides of sulfur and nitrogen, and the reaction is the basis for the well-known lead-chamber process for the manufacture of sulfuric acid.

All attempts to prepare selenium trioxide from mixtures of H_2SeO_4 and P_2O_5 have met with failure. Efforts by Worsley and Baker [*J. Chem. Soc.*, **123**, 2870 (1923)] to make it by the action of ozone on selenium dissolved in $SeOCl_2$ appear at first sight to have been successful, but this method failed in the hands of others [Meyer and Pawletta, *Ber.*, **60**, 985 (1927); Hoffman and Lehner, *J. Am. Chem. Soc.*, **51**, 3177 (1929); Smith and Mehltretter, *J. Am. Chem. Soc.*, **53**, 3562 (1931)]. A successful method for its preparation in an impure form consists of oxidation of elementary selenium by oxygen in a glow discharge excited by some 20,000 volts. The selenium is fused on a glass rod and placed between the electrodes, and oxygen at 1–5 mm is passed through the discharge tube. A white, solid mixture of SeO_2 and SeO_3 collects on the walls of the tube and on the aluminum electrodes. The percentage of SeO_3 in the mixture depends on the oxygen pressure, on the location of the deposit, and doubtless on geometrical factors. Some mixtures contain as low as 7.5% and others as high as 57% of selenium trioxide [Kramer and Meloche, *J. Am. Chem. Soc.*, **56**, 1081 (1934)].

Tellurium trioxide results from heating telluric acid strongly enough to drive off the water, the final temperature required being 300° to 360°. The trioxide so prepared is an orange-yellow solid that does not dissolve in water, dilute acids, or dilute alkali. When it is boiled with concentrated hydrochloric acid, chlorine is set free. Hot, concentrated alkalis dissolve TeO_3 to form tellurates.

At least two other oxides of sulfur exist, namely, S_2O_3 and SO_4 (and S_2O_7 [Maisin, *Bull. soc. chim. Belg.*, **37**, 326 (1928)]). The sesquioxide is formed in an energetic fashion when well-dried, powdered sulfur is added to liquid sulfur trioxide at about 15° (2–3 g S, 20 cc SO_3). The mixture forms two layers; the lower layer is a blue to blue-green solid and the upper layer is clear or has only a trace of blue color. The upper liquid layer of SO_3 can be poured off or vaporized, leaving the blue S_2O_3 in a moderately pure state. On standing at 15°, the blue sesquioxide slowly decomposes into SO_3, SO_2, and sulfur, the rate of decomposition being greater at higher temperatures; the blue color changes, as the decomposition proceeds, to green and then to brown. Sulfur sesquioxide is insoluble in SO_3, but it dissolves with a blue color if the trioxide contains some H_2SO_4 [Vogel and Partington, *J. Chem. Soc.*, **127**, 1514 (1925); Wöhler and Wegwitz, *Z. anorg. Chem.*, **213**, 129 (1933)]. A violent reaction takes place between the sesquioxide and water with the formation of H_2SO_4, H_2SO_3, polythionic acids, and sulfur.

Sulfur tetroxide, SO_4, is formed when a silent electrical discharge (6500–8000 volts) is passed through a mixture of SO_2 and O_2. The gas mixture at a total pressure of about 0.5 mm is passed through the discharge region, and the solid (white) oxide deposits on the sides of the discharge tube. Dry oxygen and sulfur dioxide are essential to prevent subsequent decomposition. The white solid varies in composition from $SO_3 \cdot SO_4$ through $SO_3 \cdot 2SO_4$ to SO_4, the pure tetroxide being the limiting substance obtainable. The SO_3—SO_4 mixture is decomposed by heat ($SO_3 + O_2$), and dissolves slowly in water. The pure or nearly pure tetroxide melts with decomposition at about 3°. It dissolves in concentrated sulfuric acid without immediate decomposition, and in this solvent the molecular weight corresponds to SO_4. In dilute sulfuric acid the substance decomposes slowly with the evolution of oxygen, and the fresh solutions react slowly with I^- to liberate iodine. Strangely enough, the aqueous solutions give no reactions indicating the presence of peroxyacids; no orange-yellow color is observed with TiO^{++} under conditions favorable for the formation of hydrogen peroxide from a peroxysulfuric acid. Further studies of the properties of SO_4 are to be desired [Meyer, Baileul, and Henkel, *Ber.*, **55**, 2923 (1922); Schwarz and Achenbach, *Z. anorg. Chem.*, **219**, 271 (1934)].

Physical properties of the oxides of S, Se, and Te

The physical properties of sulfur monoxide, SO, have already been given in the section on its preparation.

Sulfur dioxide is a substance of such importance that its properties have been investigated rather extensively. It is a colorless gas at room temperatures and pressures, but with continuous ultraviolet radiation discontinuous absorption bands are observed [Watson and Parker, *Phys. Rev.*, **37**, 1013 (1931); Price and Simpson, *Proc. Roy. Soc.*, **165**, 272 (1938)]. The region of absorption extends from 3950 Å to far into the ultraviolet. Selenium dioxide is a beautiful white solid (monoclinic crystals) which sublimes on moderate heating to give a greenish-yellow vapor, the color being due to SeO_2 and not to any free selenium, as is demonstrated by the fact that the color does not change when oxygen is present [Yost and Hatcher, *J. Am. Chem. Soc.*, **54**, 151 (1932)].

Tellurium dioxide is a white solid which does not vaporize until the temperature reaches some 450°. The dioxides of sulfur and selenium are quite soluble in water, while that of tellurium is only sparingly so. Some of the physical constants of these oxides are shown in the following table [Giauque and Stephenson, *J. Am. Chem. Soc.*, **60**, 1389 (1938); Meyer and Jannek, *Z. anorg. Chem.*, **83**, 57 (1913)]. All thermodynamic quantities given refer to one mole of sulfur dioxide.

The stability of the sulfur-group dioxides is indicated by the large free energies or heats of formation; it requires temperatures above 2000° to bring about detectable decomposition of sulfur dioxide. The vapors of sulfur and selenium dioxide consist of SO_2 and SeO_2 molecules, and not polymers of these. The structures indicated for all three dioxides have in common the feature that the gaseous molecules are not linear and that

TABLE 88

THE PHYSICAL CONSTANTS OF SO_2, SeO_2, AND TeO_2

	Melting Point (°C)	Heat of Fusion (cal)	Boiling Point (°C)	Heat of Vaporization (cal)	Density
SO_2.........	−75.46	1769	−10.02	5960	1.434 (l, 0°)
SeO_2.......	340. (under own v. pres.)	—	315. (sublimes)	21,600 (subl.)	3.95 (solid, 15°)
TeO_2........	Dull-red heat	—	—	—	5.67 (solid, 15°)

	Heat of Formation, (18°), (cal)	Free Energy of Formation (cal)	Standard Entropy (cal/deg), S°_{298}	Molecular Size and Shape	Fundamental Frequencies (cm^{-1})
SO_2	70,920	−69,660	59.40 (gas)	S—O, 1.46 Å <O—S—O, 120°	525 1152 1361
SeO_2	56,360	—	62.5 (gas)	Se—O, 1.61 Å <O—Se—O, 120°	(310) 663 790
TeO_2........	77,580	−64,320	17 4 (solid)	—	—

Vapor Pressures

$SO_2(l) = SO_2(g)$ $$\log_{10} p_{cm} = -\frac{1867.52}{T} - 0.015865T + 0.0000155747T^2$$

$SeO_2(s) = SeO_2(g)$

t (°C)	p_{mm}	t (°C)	p_{mm}
20	0	210	54.0
70	12.5	260	112.7
94	20.2	311	610.9
124	25.5	315	760.

Molal Heat Capacity of SO_2(l)

T (°K)	C_p (cal/deg)	T (°K)	C_p (cal/deg)
200	20.97	240	20.76
210	20.91	250	20.71
220	20.86	260	20.66
230	20.81		

TABLE 88 (*Cont.*)
Heat Capacity and Entropy of $SO_2(g)$

T (°K)	C_p (cal/deg)	S°_{298} (cal/deg)	T (°K)	C_p (cal/deg)	S°_{298} (cal/deg)
298.1	9.51	59.40	1000	12.90	73.09
400.	10.35	62.32	1500	13.42	78.44
500.	11.08	64.72	1800	13.56	80.90
700.	12.11	68.62			

$SO_2 \ldots P = \dfrac{RT}{v - b} - \dfrac{a}{v^2}$ $a = 6.707 \times 10^6$ atm cm^6 $b = 56.39$ cm^3

the sulfur-oxygen bond is not single but semidouble. The so-called "resonance phenomenon" is believed to enter in such a way that in the two structures O—S═O and O═S—O the double bond oscillates rapidly from one S—O bond to the other. On the average one would expect a $\frac{3}{2}$ bond, but it turns out that other factors enter (ionic and triple-bond effects) to modify this simple picture appreciably.

Of the other sulfur-group oxides, the physical properties of SO_3 are the only ones readily determinable. Tellurium trioxide is an involatile solid that decomposes into TeO_2 and O_2 on heating to a few hundred degrees. Selenium trioxide shows no decomposition at room temperatures, but whether or not it is thermodynamically stable with respect to SeO_2 and O_2 at these temperatures is not known. It dissolves readily in water to form H_2SeO_4, but tellurium trioxide will dissolve only when heated with concentrated alkali.

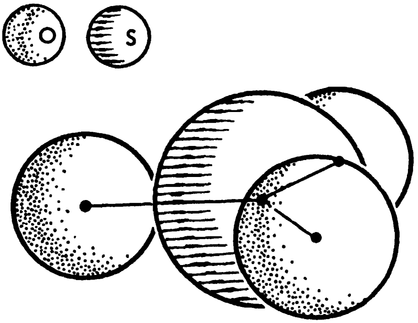

Fig. 63. The Molecular Structure of SO_3. $S—O = 1.43$Å.

Vapor-density experiments with sulfur trioxide show that monomeric molecules only are present in the gas phase. Electron-diffraction investigations show the molecules to be planar equilateral triangles with the sulfur atom at the center (Fig. 63) [Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938)]. Liquid sulfur trioxide, on the other hand, consists of a mixture of SO_3 and S_3O_9 molecules and perhaps others. Equilibrium between the two or more molecular species is attained very slowly at room temperatures, if the trioxide has been carefully dried by passing the vapors repeatedly through P_2O_5. A trace of moisture and high temperatures favor more rapid attainment of equilibrium. The Raman spectrum of the liquid indicates that the monomer, SO_3, increases in concentration with increase in temperature [Bhagarantam, *Ind. J. Phys.*, **5**, 59 (1930)]. The complexity of the liquid with the attendant slow transformations of one molecular species into another finds more than its match when the solid forms are reached. Not only does one find different solid modifications, but each modification has properties that depend on its previous history.

The solid modifications fall into three classes: first, the α or icelike modification; second, the β or low-melting asbestos-like modification; and finally, the γ or high-melting asbestos-like form. It must not be supposed that the α, β, and γ forms have the simple properties usually associated with allotropic modifications. For example, the α form will, ordinarily, melt over a range of temperatures and not isothermally. The same is true of the γ form and doubtless of the β form as well, although in this case it has not been possible to study the phenomenon thoroughly with highly dried material.

If highly dried sulfur trioxide is vaporized at room temperatures and the vapors condensed at about −80°, the resulting solid consists of the α ice-like form. (If not highly dried, the condensed vapors consist of both the α and the β form, the latter constituting about three-fourths of the total material.) The vapor pressure of the highly dried α form increases with temperature until melting begins (about 11.5°) and then decreases until all of the material has melted, the latter point being around 17°, Curve I, Fig. 64. If the liquid is now kept at 18° for about 18 hours and then cooled to 0°, the resulting solid has, at the same temperatures, lower vapor pressures than those found in the first experiment. If the liquid is again kept at 18° for 40 hours, then cooled to 0° and the vapor pressures determined once more, Curve III is obtained, the vapor pressures being lower than those found in the second experiment. If now some of the liquid or solid is distilled off, the residue would show a vapor-pressure curve such as IV, V, or VI. These curves were obtained by distilling off successive portions and determining the vapor pressure of the residue in each case.

These results for the α form may be explained by assuming that the liquid phase contains at least two molecular species (polymers) of the trioxide, say $(SO_3)_m$ and $(SO_3)_n$, and that the solid is a solid solution of these in still another species, $(SO_3)_{m+n}$. It must be assumed further that the reaction $n(SO_3)_m = m(SO_3)_n$ is slow but reversible and that one of the polymers is more volatile than the other. Also, in the solid phase the slow reversible reactions $(SO_3)_{m+n} = (SO_3)_m + (SO_3)_n$ and $n(SO_3)_m = m(SO_3)_n$ must be supposed possible. In the highly dried material the reactions are so slow that they can be regarded, for practical purposes, as not taking place at all, and those in the liquid phase would require weeks for equilibrium to be attained. If a catalyst is present, such as a trace of moisture, equilibrium is attained much more rapidly and the limiting vapor-pressure curve is obtained. For this equilibrium, solid and liquid, the triple point is sharp and lies at 16.8°; that is to say, when the constituent molecular species in the solid, liquid, or solid-liquid mixture are in equilibrium with each other, then sulfur trioxide behaves like more familiar substances (*e.g.*, water and ice). When equilibrium conditions do not obtain, the liquid acts like a solution of two components, and the solid behaves like a solid solution [see G. N. Lewis, *J. Am. Chem. Soc.*, **45**, 2836 (1923), for the theory of such systems].

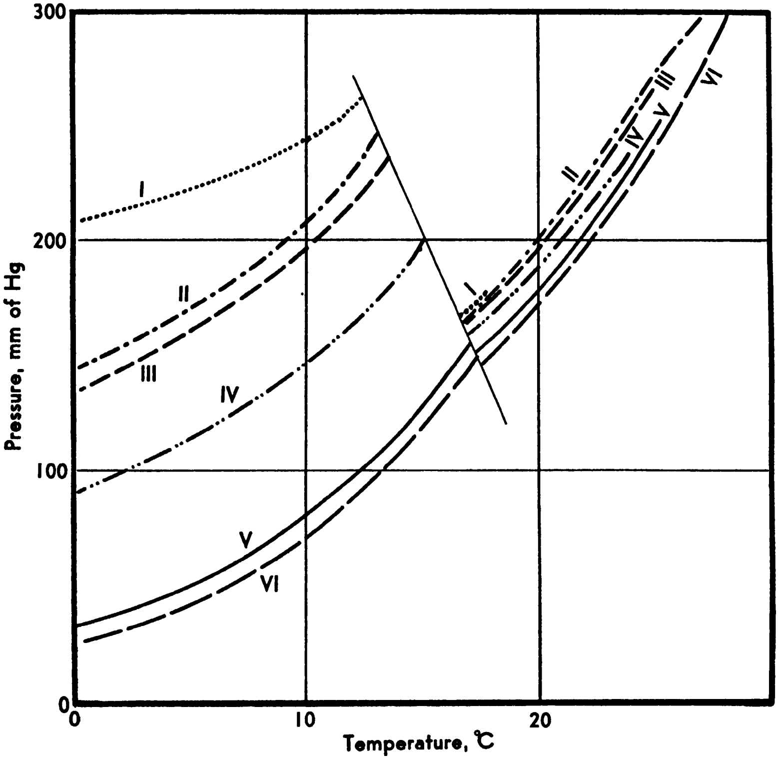

Fig. 64. Curves Showing the Vapor Pressure of Highly Dried Sulfur Trioxide and How It Varies with Aging and Partial Evaporation of the Sample. Between the measurements represented by the curves I and II, and II and III, the molten material was allowed to stand 18 and 40 hours, respectively. Between III and IV, IV and V, and V and VI, portions of the sample were distilled away. [Smits and Schoenmaker, *J. Chem. Soc.*, **125**, 2554 (1924).]

The β form is obtained only with difficulty from highly dried sulfur trioxide. When ordinary sulfur trioxide is distilled and the receiver cooled so that the solid collects, both the α form and the β form result. The more volatile α form may be distilled off from the mixture, and the less volatile residue that remains consists of the β form. Since this material is not highly dried, equilibrium between the various molecular species is attained with little difficulty. The equilibrium β form melts at 32.5°. The fact that the vapor pressures of the equilibrium β form are lower than those of the α form shows that the former is the more stable at room temperatures, and this is in accord with the fact that, at room temperatures, the liquid trioxide containing a trace of moisture eventually solidifies with the formation of the β form. The additional fact that some α form is found along with the β form indicates, possibly, that the water catalyst goes into the solid β form until the liquid is too dry to come to equilibrium rapidly.

The γ form is prepared by allowing sulfur trioxide vapors to condense at liquid-air temperatures. The vapor pressure of the solid is much lower than that of the α or β form at the same temperature. That the γ form is not simple is shown by the fact that at 50° the vapor pressure becomes constant only after ten months, during which time the pressure rises from 15 cm and approaches 65 cm asymptotically. When melting begins, equilibrium is attained much more rapidly in the liquid phase than in the solid. Indeed, if the solid is warmed up at a moderate rate to about 95°, the vapor pressure can change, when melting begins, from three to nine atmospheres in a short interval of time. Such an experiment is accordingly accompanied by some danger. When heated up under equilibrium conditions, the melting point of the γ form of sulfur trioxide is 62.2°. The careful investigation of carefully dried sulfur trioxide is due to Smits and Shoenmaker [*J. Chem. Soc.*, **129**, 1108 (1926) *et ante*]. Further experiments on the ordinary liquid were made by Grau and Roth [*Z. anorg. Chem.*, **188**, 173 (1930)].

The nature of the molecular species present in liquid and solid sulfur trioxide has not been fully investigated; the Raman spectrum of the liquid indicates that at higher temperatures, $\sim$ 100°, SO_3 is the predominant substance and at lower temperatures, $\sim$ 20°, S_3O_9 is present at appreciable concentration [Gerding, Nijveld, and Muller, *Z. phys. chem.*, **B 35**, 193 (1937)].

The physical properties of sulfur trioxide are shown in Table 89. The vapor pressures presented refer to the limiting or equilibrium states. For non-equilibrium states, Fig. 64 may be consulted.

The structure of the SO_3 molecule in the gaseous state is, as remarked above, simple, the oxygen atoms being at the corners and the sulfur atom at the center of an equilateral triangle. On the basis of the octet theory of valency, the S—O bonds would be three in number, each consisting of a single electron pair. It turns out, however, that the bonds have some ionic character; and as a result of this and other effects not

TABLE 89
THE PHYSICAL PROPERTIES OF SULFUR TRIOXIDE
Vapor Pressures (Equilibrium)

Solid, α		Liquid, α	
t (°C)	p_{mm}	t (°C)	p_{mm}
0.15	45.5	17.6	166.4
5.0	66.0	22.5	225.9
10.2	85.5	35.0	460.7
		40.5	603.9
		45.0	777.2
		74.0	2964.0

Heat of sublimation (16.8°), 11,900 cal.
Heat of evaporation (16.8°), 10,000 cal.
Heat of fusion (16.8°), 1800 cal.

Solid, β		Liquid, β	
t (°C)	p_{mm}	t (°C)	p_{mm}
0.2	33.0	20.3	162.8
5.1	49.2	30.3	334.1
10.1	72.3	35.0	460.7
		45.0	777.2
		74.0	2964.0

Heat of sublimation (32.5°), 13,000 cal.
Heat of evaporation (32.5°), 10,100 cal.
Heat of fusion (32.5°), 2900 cal.

Solid, γ		Liquid, γ	
t (°C)	p_{mm}	t (°C)	p_{mm}
30	120	65.4	2441.0
40	290	74.0	2964.0
50	650	80.9	3985.5
		90.2	5794.0

Heat of sublimation (62.2°), 16,300 cal.
Heat of evaporation (62.2°), 10,100 cal.
Heat of fusion (62.2°), 6200 cal.

TABLE 89 (*Cont.*)
Liquid (Equil.) (Roth)

t (°C)	p_{mm}	t (°C)	p_{mm}
15.00	153.0	35.00	466.5
20.00	208.5	40.00	605 5
25.00	272.0	44 5	770.0
30.00	355.0		

Heat of vaporization, 10,160 cal.
Heat of vaporization (Exp.), 10,000 cal.

Density	Surface Tension (l) (dynes/cm)	Dielectric Constant (l)	Heat of Formation (cal)	Free Energy of Formation, ΔF^0_{298} (cal)	Standard Entropy, S^0_{298} (cal/deg)
1.904	34.17 (19°)	3.64(19°)	93,900(g) 106,000(α) 105,200(β)	−85,890(g)	61.19(g)

Fundamental frequencies (cm^{-1}), 1068, 1330, 530, 560(2); 560(2) doubly degenerate.
Structure S—O, 1.43 Å. O—S—O angle = 120°.

well understood, the S—O distance is smaller than would be predicted for a single bond [Palmer, *loc. cit.*].

Chemical properties

Sulfur dioxide acts as an excellent reducing agent and its applications often depend on this fact. Most of the reducing reactions of interest take place in aqueous solution. Its gaseous or gas-solid reactions are typified by those with the halogens, $SO_2 + X_2 = SO_2X_2$. But it may also act as an oxidizing agent, as in the reactions

$$2SO_2(g) + 4H_2(g) = S_2(g) + 4H_2O(g)$$
$$2SO_2(g) + 4CO(g) = S_2(g) + 4CO_2(g)$$

which take place at 1000° or higher. Sulfur dioxide at low temperatures readily forms solid complex salts with solid iodides or thiocyanates. With potassium iodide the red compounds $KI(SO_2)_2$ and $KI(SO_2)_4$ are known, while with thiocyanates bright-yellow complexes containing $\frac{1}{2}SO_2$ or one SO_2 per thiocyanate ion have been prepared [Ephraim and Kornblum, *Ber.*, **49,** 2007 (1916)]. Sulfur dioxide is more soluble in alcohol, camphor, formic acid, acetone, and concentrated sulfuric acid than in water, the approximate volumes absorbed at 25° being, respectively, 84.2, 300, 351, 589, 6, and 30 at atmospheric pressure. Elementary sulfur will not dissolve in liquid SO_2.

Selenium dioxide, in contrast to sulfur dioxide, is a good oxidizing agent. The solid exposed to air eventually becomes pink to red in color as the result of its reduction to elementary selenium by organic dust particles. As a reducing agent it is not strong, and only fluorine is able to oxidize it to SeO_2X_2. Substances such as concentrated H_2O_2, molten Na_2O_2, and $KMnO_4$ are able to oxidize the dioxide to selenates. When the dry dioxide is left exposed to the atmosphere, it absorbs water to form the white crystalline acid H_2SeO_3. The dioxide dissolves readily in water to form solutions of selenious acid, H_2SeO_3.

Tellurium dioxide is comparatively unreactive. It may be reduced to elementary tellurium by hydrogen at elevated temperatures. When heated with strong (30%) H_2O_2 and sulfuric acid, it is converted to telluric acid.

Sulfur trioxide is very reactive indeed. It reacts with organic matter to form sulfonic acid derivatives or to form carbon and sulfur dioxide; intermediate stages of oxidation of organic substances are common. Sulfur trioxide reacts with some solid halides to liberate the free halogen, this being especially the case with iodides. In the liquid form it combines directly with NO_2 to form oxynitrososulfuric anhydride, $(NO_2SO_3)_2$, a white solid which on heating gives up oxygen to form $(NO)_2S_2O_7$. The reactivities of the α and β forms of solid sulfur trioxide are not the same. Thus, with PCl_5 the α form reacts to give SO_2, Cl_2, $POCl_3$, and $S_2O_5Cl_2$, but the β form yields $POCl_3$ and $S_2O_5Cl_2$ alone. Carbon tetrachloride reacts rapidly with the α and slowly with the β form, the reaction being

$$2SO_3 + CCl_4 = S_2O_5Cl_2 + COCl_2$$

Sulfur trioxide reacts energetically with basic oxides to form sulfates. With water the reaction is so vigorous that solution is accompanied by a hissing noise and a large evolution of heat. It combines with water in all proportions to form a series of hydrates of sulfuric acid and solutions of the latter in water.

The reactivity of selenium trioxide has not been much investigated. It is hygroscopic and dissolves readily in water to form selenic acid. The orange-yellow tellurium trioxide is slow to react with water and is dissolved only by boiling with strong alkalis. It decomposes into TeO_2 and O_2 when heated to a few hundred degrees.

The Oxyacids of Sulfur, Selenium, and Tellurium

When the oxides of the sulfur-group elements dissolve in water, acids are formed, that is, substances that ionize to give hydrogen ion H^+ or hydronium ion H_3O^+. Some of the oxides are known as acid anhydrides, these being substances which react with water reversibly as follows:

$$\text{Anhydride} + \text{Water} = \text{Acid}$$

Other oxides, S_2O_3, for example, do not appear to be acid anhydrides, since the products of their reaction with water are not simply acids, but nonacidic substances as well. Conversely all oxyacids are not formed from anhydrides and water; indeed, the anhydride may not exist. Thus there are no known anhydrides of dithionic, thiosulfuric, and the polythionic acids.

The sulfur-group oxides that are definitely acid anhydrides are SO_2, SO_3, SeO_2, SeO_3, TeO_2, and TeO_3, and they form, respectively, the acids:

H_2SO_3	Sulfurous	H_2SeO_3	Selenious	H_2TeO_3	Tellurous
H_2SO_4	Sulfuric	H_2SeO_4	Selenic	H_6TeO_6	Orthotelluric

This list does not by any means contain all of the known oxyacids of sulfur, selenium, and tellurium. Moreover, there are salts for which the corresponding acid does not exist; thus normal tellurates, for example, K_2TeO_4, are known, but it is doubtful if other than the free orthotelluric acid, H_6TeO_6, exists, although the so-called allotelluric acid may be $(H_2TeO_4)_n$. The following list contains all of the definitely established oxyacids of S, Se, and Te. In the cases where the free acid is not known but only the salts of it, the fact is indicated by giving the formula of a known salt of the acid in parentheses. In each case a method of preparation of the acid or a salt of it is stated after the name of the acid.

THE OXYACIDS OF S, Se, AND Te

S		
	H_2SO_2	($ZnSO_2$) Sulfoxylic. $SO_2Cl_2 + Zn$ in ether solution.
	$H_2S_2O_4$	Hyposulfurous. $NaHSO_3$ (aq) + Zn.
	H_2SO_3	Sulfurous. SO_2 + water.
	$H_2S_2O_5$	($K_2S_2O_5$) Pyrosulfurous From soln. $KHSO_3 + SO_2$.
	$H_2S_2O_6$	Dithionic. SO_2 + aq. suspension MnO_2.
	H_2SO_4	Sulfuric. SO_3 + water.
	$H_2S_2O_7$	Pyrosulfuric. $SO_3 + H_2SO_4$ (100%). Salts, *e.g.*, $Na_2S_2O_7$, formed by strongly heating $NaHSO_4$.
	$H_2S_2O_3$	($Na_2S_2O_3$) Thiosulfuric. $Na_2SO_3 + S$.
	H_2SO_5	Peroxymonosulfuric. 30% H_2O_2 + conc. H_2SO_4
	$H_2S_2O_8$	Peroxydisulfuric. Electrolysis of $KHSO_4$ solns.
	$H_2S_nO_6$	Polythionic, $n = 3, 4, 5, 6$. In Wackenroder's soln., $SO_2 + H_2S$ + water.
Se		
	H_2SeO_3	Selenious. SeO_2 + water.
	H_2SeO_4	Selenic. $H_2SeO_3 + Cl_2$; $Ag_2SeO_3 + Br_2 + H_2O$.
Te		
	H_2TeO_3	Tellurous. TeO_2 only slightly soluble in water. Acid is very weak.
	H_6TeO_6	Orthotelluric. Reflux TeO_2, conc. H_2SO_4 and 30% H_2O_2. Purify H_6TeO_6 by crystallization.
	$H_xTe_yO_z$	Polytelluric. Salts, *e.g.*, $K_2Te_4O_{13}$, by heating $K_2H_4TeO_6$.
	H_2TeO_4	(?) Allotelluric. Melt H_6TeO_6. Sirupy and soluble in water in all proportions.

Sulfurous, selenious, and tellurous acids

The oxyacids for which acid anhydrides are well known are more commonly encountered and are of greater practical importance than the others, although not necessarily more interesting. It is convenient to discuss this group of acids first, if for no other reason than that their properties have been investigated more thoroughly.

Sulfur dioxide dissolves readily in water to form solutions of H_2SO_3. When the partial pressure of the gas above the solution is 760 mm, the concentration is 1.34 m at 25°; at 0° the saturated solution is 3.55 m and at 40° 0.84 m. The acid is weak and the second hydrogen ionizes less freely than the first. As a result of this fact, both normal and acid salts may be prepared. The two ionization constants are as follows [Sherrill and Noyes, *J. Am. Chem. Soc.*, **48,** 1861 (1926); Kolthoff, *Chem. Weekblad*, **16,** 1154 (1919); Tartar and Garretson, *J. Am. Chem. Soc.*, **63,** 808 (1941)]:

$$H_2SO_3 = H^+ + HSO_3^- \qquad \frac{(H^+)(HSO_3^-)}{(H_2SO_3)} = 0.0172 \text{ at } 25^\circ$$

$$HSO_3^- = H^+ + SO_3^= \qquad \frac{(H^+)(SO_3^=)}{(HSO_3^-)} = 6.24 \times 10^{-8} \text{ at } 25^\circ$$

The free acid H_2SO_3 has not been prepared; when a concentrated solution of sulfurous acid is cooled strongly, crystals of the hydrate $SO_2 \cdot 7H_2O$ separate out.

The alkali metal sulfites and acid sulfites are, with the exception of $NaHSO_3$, moderately soluble in water. The solubility of sodium sulfite increases with temperature up to 33°, after which it decreases. Because of the weakly acid character of sulfurous acid, the salts are hydrolyzed in solution; an alkali sulfite solution is basic, an acid sulfite (bisulfite) solution is slightly acid. Accordingly one would predict, and experiment shows, that when an acid sulfite solution is boiled, sulfur dioxide comes off until the solution contains mostly $SO_3^=$. Nice crystals of alkali sulfites may be obtained by warming bisulfite solutions. The alkaline earth sulfites are only slightly soluble, but they dissolve readily on the addition of a strong or moderately strong acid and even in sulfurous acid itself. This effect is due to the formation of the soluble weak acid H_2SO_3.

$$MgSO_3 + 2H^+ + SO_4^= = H_2SO_3 + Mg^{++} + SO_4^=$$

The solid, alkaline earth bisulfites have never been prepared; they undoubtedly exist in solution, since the solubilities of the sulfites are greatly increased by dissolving SO_2 in their saturated solutions. In solution the sulfites of trivalent chromium, aluminum, indium, gallium, and other weakly basic substances are strongly hydrolyzed, and as a consequence only basic sulfites are obtained on the evaporation of the solutions.

$$Al^{+++} + SO_3^{=} + H_2O = AlO^+ + HSO_3^- + H^+$$

Sulfites form complexes (coordination compounds) or weak electrolytes with many of the heavy metal salts. Thus when H_2SO_3 is added to a dilute sulfuric acid solution of Fe^{+++}, the almost colorless solution becomes red in color owing to the formation of a complex ion or weak salt; with time the intensity of the color decreases as a result of the reduction of the ferric to ferrous iron. With gold the salts $M_3Au(SO_3)_2$ and $M_5Au(SO_3)_4$ are known, each sulfite radical occupying one coordination position. The same coordination number is shown in the compound $Na_5Fe(CN)_5SO_3$, which is derived from $Na_4Fe(CN)_6$ by replacing a cyanide by a sulfite radical. On the other hand, in some platinum compounds, for example, $K_3PtCl_3SO_3$, $K_4PtCl_2(SO_3)_2$, and $K_3PtCl(SO_3)_2$, the sulfite radical occupies sometimes one and sometimes two coordination positions, since bivalent platinum has, in general, a coordination number of four.

Sulfurous acid and its salts act as excellent and cheap reducing agents. Oxygen itself oxidizes them slowly, and as a consequence solutions of the acid or its salts always contain sulfates unless care is exercised to exclude air. In the presence of some reducing agents, for example, Fe^{++} and $AsO_3^{=}$, sulfites are much more rapidly oxidized by oxygen than in the absence of these substances. If a mixture of air and sulfur dioxide is bubbled into a dilute solution of 0.05 m ferrous or ferric sulfate or chloride, sulfuric acid is formed, and in the course of a few hours concentrations of the acid exceeding one molal may be attained. The mechanisms of these reactions are not well understood. Since two reducing agents are essential, it must be that oxygen combines with both simultaneously to form a reactive intermediate. In mixtures of sulfite and arsenite, both are simultaneously oxidized by oxygen and the mixture is oxidized much more rapidly than either component when present alone.

$$\left.\begin{matrix} AsO_3^{\equiv} \\ \\ SO_3^{=} \end{matrix}\right\} + O_2 = \left\{\begin{matrix} AsO_3O^{\equiv} \\ \\ SO_3O^{=} \end{matrix}\right\} = AsO_4^{\equiv} + SO_4^{=}$$

Whether these intermediates are peroxyacids or not is not known, but it would be worth while to settle the question one way or the other.

There are other substances that *inhibit* the oxidation of sulfites by oxygen; for example, small concentrations of phenol, glycerine, mannitol, benzaldehyde, and especially stannous chloride will greatly decrease the rate of conversion to sulfate.

The halogens oxidize sulfurous acid or sulfite solutions quantitatively and rapidly to sulfate. The reactions are not so simple in the case of the oxidizing agents Fe^{+++}, RuO_4, MnO_2, $KMnO_4$, and doubtless many others; along with sulfate, dithionate is also formed with these agents. Since the relative amount of dithionate formed is dependent on concentrations and temperature, it is not possible to use some oxidizing agents, for example, $KMnO_4$ and H_2O_2, for the quantitative estimation of sulfites. In the case of MnO_2 the equation for the reaction is MnO_2 (aq. susp.) $+ 2H_2SO_3 = S_2O_6^= + Mn^{++} + 2H_2O$, although it must be understood that sulfate is also formed at the same time by the reaction

$$MnO_2 + H_2SO_3 = Mn^{++} + SO_4^= + H_2O$$

A striking lecture experiment involving the oxidation of sulfites, and one that delights even the old hands at chemistry, is that offered by the Landolt reaction. In acid solution sulfites are oxidized by iodates, the products of the reaction being iodide and sulfate.

$$3H_2SO_3 + IO_3^- = 3SO_4^= + I^- + 3H_2O$$

Iodate also reacts fairly rapidly with iodide in acid solution to form iodine,

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O$$

but the liberated iodine reacts at a very rapid rate with sulfite.

$$H_2SO_3 + I_2 + H_2O = SO_4^= + 2I^- + 4H^+$$

This last reaction is so rapid that no color of iodine is observed until all of the sulfite has been oxidized. At that point, especially if a little starch has been added, the solution suddenly becomes blue. Since the time necessary for the blue color to appear is a function of temperature and concentrations, the reaction may be used as a clock. Landolt found that the time in seconds from the time of mixing to the time of appearance of color can be represented empirically by the following formula [Landolt, *Ber.*, **20,** 745 (1887)],

$$T_{sec} = \frac{906.05 - 23.01t + 0.1888t^2}{C_s^{0.904} C_I^{1.642}}$$

where C_s and C_I are the concentrations of H_2SO_3 and HIO_3 expressed in moles per cubic meter of solution, and t is the temperature in degrees centigrade.

Sulfurous acid may also act as an oxidizing agent. Thus in Wackenroder's solution H_2S is oxidized to elementary sulfur by H_2SO_3; in addition to this reaction there are a number of side reactions leading to the formation of thiosulfate and polythionates. In acid solutions iodides are oxidized slowly to iodine,

$$4I^- + H_2SO_3 + 4H^+ = 2I_2 + S + 3H_2O$$

but since aqueous iodine and sulfurous acid react rapidly to form sulfate and iodide ions, the net effect is the catalytic decomposition of sulfurous acid.

$$3H_2SO_3 = 4H^+ + 2SO_4^{=} + S + H_2O$$

The sulfur does not precipitate immediately but remains in solution as either a yellow colloidal sulfur or as a complex ion formed with the iodide or sulfite or both. Sulfurous acid is also reduced by zinc. When a solution of H_2SO_3 is poured through a Jones reductor (a glass tube provided with a stopcock at the lower end and filled with granulated zinc), the resulting unstable solution has an intense yellow color and acts as a very strong reducing agent. The yellow solution contains, among other substances, hyposulfurous acid, $H_2S_2O_4$.

The ability of sulfurous acid to act as a reducing agent and to fill coordination positions in inorganic and organic compounds is doubtless a factor in its action as an agent for killing bacteria and yeasts. Sulfur dioxide, from burning sulfur, is sometimes used as a fumigant. In the manufacture of wine, the addition of a small amount of SO_2 to the *must* serves to kill bacteria, molds, and wild yeasts without materially retarding the multiplication of yeasts that are effective in the alcoholic fermentation. From 75 to 270 grams of SO_2 per thousand liters of *must* is the quantity usually used [Joslyn and Cruess, *Circular* 88, *Cal. Agr. Ext. Serv.*, 1934]. The effect of sulfurous acid or sulfur dioxide on the lungs appears to be one such that resistance to bad colds is decreased; those susceptible to colds should avoid breathing the gas.

Selenium dioxide absorbs water to form the solid, white, selenious acid, H_2SeO_3. The reaction is readily reversible at ordinary temperatures, as the following dissociation pressures show.

TABLE 90

THE DISSOCIATION PRESSURES OF H_2SeO_3

$H_2SeO_3(s) = SeO_2(s) + H_2O(g)$

Temp (°C)	Press. of $H_2O(g)$ (mm)	Temp. (°C)	Press. of $H_2O(g)$ (mm)
20	0.8	50	10.5
30	2.0	60	21.2
40	4.6	70	44.6

These results explain why solid selenious acid loses water on hot, dry days.

Selenious acid, H_2SeO_3, is remarkably soluble in water. The following table contains the molal concentrations of H_2SeO_3 in saturated solutions in equilibrium with $H_2SeO_3(s)$ [Ishikawa and Abe, *Sci. Papers Inst. Phys. Chem. Res. Japan*, **34**, 775 (1938)]. Above 70° the solid phase changes to $SeO_2(s)$.

TABLE 91

SOLUBILITY OF $H_2SeO_3(s)$ IN WATER

Temp. (°C)	Conc. Moles H_2SeO_3 per 1000 g H_2O	Temp. (°C)	Conc. Moles H_2SeO_3 per 1000 g H_2O
20	(20)	50	53.7
30	33.5	60	89.1
40	44.5	70	176.3

Selenious acid is weaker than sulfurous acid [Blanc, *J. chim. phys.*, **18,** 28 (1920); Hagisawa, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **18,** 648 (1939)], but much stronger than the more common acetic, benzoic, and carbonic acids.

$$H_2SeO_3 = H^+ + HSeO_3^- \qquad \frac{(H^+)(HSeO_3^-)}{(H_2SeO_3)} = 2.4 \times 10^{-3} \text{ at } 25°$$

$$HSeO_3^- = H^+ + SeO_3^= \qquad \frac{(H^+)(SeO_3^=)}{(HSeO_3^-)} = 4.8 \times 10^{-9} \text{ at } 25°$$

Both the normal and the acid salts can be prepared readily. The alkali metal selenites and acid selenites are moderately soluble. Of interest is the rather insoluble silver selenite, Ag_2SeO_3, which forms when a soluble silver salt is added to a selenite solution. It is soluble in strong acids and is somewhat soluble in selenious acid itself; when treated with bromine or chlorine water, it is converted into H_2SeO_4 and insoluble AgBr or AgCl.

Selenious acid is an oxidizing agent but not a very strong one. It oxidizes iodide ion to iodine, but has no effects on bromide or chloride ion. The reaction with iodide ion is reversible [Schott, Swift, and Yost, *J. Am. Chem. Soc.*, **50,** 721 (1928)].

$$H_2SeO_3 + 4H^+ + 4I^- = Se(s) + 2I_2(s) + 3H_2O$$

$$K = \frac{1}{(H^+)^4(I^-)^4(H_2SeO_3)} \qquad \frac{1}{K} = 1.46 \times 10^{-14} \text{ at } 25°$$

In this equilibrium expression, (H^+) and (I^-) represent the activities of these ions and not simply their concentrations. It is evident from the value of K that when, for example, $(H^+) = (I^-) = 0.1$, the concentration of H_2SeO_3 is very small indeed. Accordingly, in acid iodide solutions, the reaction may be made the basis for the volumetric estimation of selenious acid or selenium. There is no compound formed when iodine and selenium are mixed alone or in the presence of aqueous solutions at room temperatures; but there is evidence for compound formation, Se_2I_2, in carbon tetrachloride solution when this solvent is shaken with a mixture of selenium and iodine.

Selenious acid solutions are readily reduced to elementary selenium when treated with sulfurous acid. The precipitated selenium is red in color. On heating, the filtered precipitate becomes black in color and shows an inclination to exist in a viscous liquid state until freed from contaminating substances. There is an indication that the precipitate contains sulfuric or sulfurous acid. This is driven off by heat. The latter phenomenon is more noticeable with concentrated solutions than with dilute ones. The precipitation of selenium from dilute solutions of H_2SeO_3 with H_2SO_3 forms the basis of an analytical procedure in which the selenium is weighed as such.

In dilute hydrochloric acid solution, selenious acid shows no tendency to form chlorides. Concentrated hydrochloric acid solutions of it contain appreciable concentrations of the tetrachloride or oxychloride. When such solutions are boiled, the selenium-chlorine compound volatilizes and the whole of it may be distilled out. When strong hydrochloric acid solutions of selenious acid are shaken with elementary selenium, a red liquid settles out until equilibrium is established; the red liquid is, presumably, Se_2Cl_2.

Since tellurium dioxide is only sparingly soluble in water, only the solid H_2TeO_3 or very dilute solutions can be prepared. Alkali tellurites are known, and solutions of them are easily prepared by dissolving the dioxide in an alkali such as sodium or potassium hydroxide. Tellurium dioxide dissolves in strong acids to form the positive ion $TeOOH^+$ [Schuhmann, *J. Am. Chem. Soc.*, **47**, 356 (1925)]. The acidic and basic ionization constants at 25° are [see also Blanc, *J. chim. phys.*, **18**, 28 (1920)],

$$\begin{aligned} H_2TeO_3 &= H^+ + HTeO_3^- & K_1 &= 2 \times 10^{-3} \\ HTeO_3^- &= H^+ + TeO_3^{=} & K_2 &= 10^{-8} \\ H_2TeO_3 &= TeOOH^+ + OH^- & K &= 10^{-11} \\ TeO_2 + H^+ &= TeOOH^+ & K &= 8.9 \times 10^{-3} \end{aligned}$$

The oxidation potential of acid solutions of tellurium dioxide is, in accordance with the statement regarding the ion present, represented as follows [Schuhmann, *loc. cit.*],

$$Te(s) + 2H_2O = TeOOH^+ + 3H^+ + 4E^-, \qquad E^\circ_{298} = -0.559 \text{ volts}$$

Inasmuch as the common reducing agents H_2SO_3 and Sn^{++} have appreciably higher oxidation potentials, they will reduce $TeOOH^+$ to metallic tellurium. The halogens and Fe^{+++}, on the other hand, will oxidize elementary tellurium to $TeOOH^+$ in the presence of strong acids.

Sulfuric, Selenic, and Telluric Acids

Preparation of sulfuric acid

There are two important processes by which sulfuric acid is prepared commercially. In the first and most important, the contact process, nearly dry, hot oxygen and sulfur dioxide are caused to combine in the presence of a vanadium pentoxide catalyst to form sulfur trioxide, as described in a previous section. The sulfur trioxide is dissolved in 98% sulfuric acid to obtain 99.5% acid, or the fuming acid known as "oleum," $H_2SO_4{\cdot}SO_3$. The sulfur dioxide used is obtained either by burning brimstone or as a by-product from the roasting of sulfide ores (ZnS, PbS). After removing smoke particles of arsenic trioxide and other solids in a Cottrell electrical precipitator, the sulfur dioxide-air mixture (5 to 7% SO_2) is heated finally to some 600° in heat interchangers and is then caused to pass through a converter of parallel tubes containing the vanadium catalyst. As much as eleven tons of catalyst may be contained in a single converter. The heat of the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$ is employed in the heat interchangers to heat the incoming gases.

The high concentration acid formed from sulfur trioxide varies in strength depending on the purpose for which it is meant. If used in fertilizer manufacture, the 99.5% acid is diluted to 93% strength and then either treated with synthetic ammonia to form ammonium sulfate or used to convert phosphate rock to phosphoric acid [Cobleigh, *Ind. Eng. Chem.*, **24,** 717 (1932)].

The second or lead-chamber process depends upon the fact that nitric oxide acts as a catalyst for the reaction between sulfur dioxide, oxygen, and water vapor to yield eventually dilute sulfuric acid. From a chemical point of view, the reactions in the contact process are simple, but those in the lead-chamber process are complex, and there is not unanimity of opinion concerning their mechanisms. The lead-chamber process produces cheaply dilute sulfuric acid of 62 to 77% strength; if stronger acid is desired, a rather costly evaporation must be carried out. The latter is effected most easily and economically with dilute acids of any origin by bubbling hot gases from an oil burner through a succession of tanks of the acid, the last tank containing the weakest acid [Spangler, *Ind. Eng. Chem.*, **21,** 417 (1929)].

In the lead-chamber process, the sulfur dioxide-air mixture obtained by burning brimstone or iron pyrites is passed in succession upward through the Glover tower, through two or more large lead chambers, and finally upward through the Gay-Lussac tower, as indicated in Fig. 65. The Glover tower is 20 to 25 feet high and is partly filled with acid-resisting rocks, through which passes acid sprayed in at the top of the tower;

the acid used comes from the bottom of the Gay-Lussac tower. The Gay-Lussac tower is 40 to 50 feet high and is filled with pieces of coke or acid-resisting rock, over which trickles acid sprayed in at the top; this acid comes from the bottom of the Glover tower. The sulfuric acid entering the Glover tower contains nitrosyl bisulfate (nitrosyl sulfonic acid), $ONHSO_4$; and when this meets the sulfur dioxide-air mixture, the following reaction takes place:

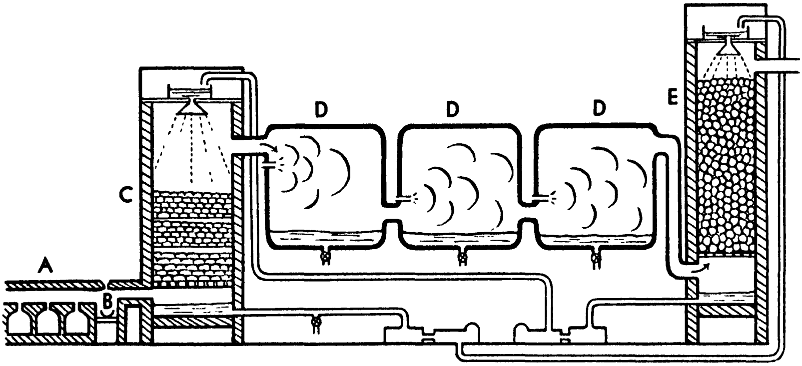

Fig. 65. The Lead Chamber Process. *A*, sulfur of pyrite burners; *B*, the nitre pot for the introduction of oxides of nitrogen (this is now generally replaced by an ammonia oxidation unit); *C*, the Glover tower; *D*, the lead chambers; *E*, the Gay-Lussac tower.

$$2ONHSO_4 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$
$$2NO + 2SO_2 + \frac{3}{2}O_2 + H_2O = ONHSO_4$$

Some 16% of the total acid formed in the lead-chamber process is produced in the Glover tower. The reactive gases that enter the lead chambers consist of SO_2, O_2, NO, and NO_2, and here they are mixed with steam or a spray of water; this mixture reacts according to the equations[1]

$$NO + \frac{1}{2}O_2 = NO_2$$
$$2SO_2 + 3NO_2 + H_2O = 2ONHSO_4 + NO$$
$$2ONHSO_4 + H_2O = 2H_2SO_4 + NO + NO_2$$

The spent gases containing NO, NO_2, and O_2 now enter the Gay-Lussac

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[1] Sulfur dioxide reacts very slowly with nitrogen dioxide at ordinary temperatures to form the solid, colorless compound $S_2N_2O_9$; the structural formula of this compound has not been established, but in composition it corresponds to the anhydride of $NOHSO_4$, that is, $ONSO_3OO_3SNO$. The reaction $2SO_2(g) + 3NO_2(g) = S_2N_2O_9(s) + NO$ is catalyzed by platinized asbestos. When heated at 400° to 500°, $S_2N_2O_9$ decomposes reversibly into S_2NO_7 and NO_2 [Briner, Lunge, and van der Wijk, *Helv. Chim. Acta*, **11**, 1125 (1928); see also Jones, Price, and Webb; *J. Chem. Soc.*, 312 (1929)].

tower, where the following reaction takes place with the acid trickling through it:

$$2H_2SO_4 + NO + NO_2 = 2ONHSO_4 + H_2O$$

This reaction is the reverse of one of the reactions taking place in the lead chambers, and in order that the absorption of the NO and NO_2 may be complete, the sulfuric acid in the Gay-Lussac tower must be fairly concentrated; ordinarily it is from 78 to 82% in H_2SO_4. It is this 78 to 82% acid containing $ONHSO_4$ that is pumped to the top of the Glover tower, where it eventually reacts with the incoming sulfur dioxide-air mixture as already described. The lead-chamber process is therefore cyclic in nature; the nitrogen oxides act as catalysts and are not, in principle, consumed. Actually there is some loss due to incomplete absorption in the Gay-Lussac tower, and this loss is made up by adding nitrogen oxides obtained by burning ammonia at the surface of a platinum gauze catalyst (Parsons catalyst).

Still another reaction of importance takes place in the Gay-Lussac tower, namely,

$$H_2SO_4 + N_2O_4 = ONHSO_4 + HNO_3$$

The nitric acid reacts, in the Glover tower, with sulfur dioxide to form nitrogen oxides or nitrosyl bisulfate and hence is not lost.

The temperatures prevailing in the lead chambers vary from 65° to 30° and are not constant throughout any one chamber. In the Glover tower, the temperature is permitted to reach about 130°, which suffices to concentrate the acid to the 78 to 82% strength necessary in the Gay-Lussac tower.

The acid produced in the lead-chamber process is drawn off from the bottoms of the lead chambers and the Glover tower. It contains about 77% H_2SO_4 and in addition small amounts of impurities, mainly nitric and nitrous acid, arsenious oxide, selenious acid, and lead sulfate, together with smaller amounts of iron, copper, zinc, mercury, and antimony. In some applications these impurities are not harmful; in others, for example, storage batteries, they are harmful and must be removed. Moreover, 77% acid is not sufficiently concentrated for many purposes (petroleum products purification requires 98-93% acid), and consequently it must be subjected to evaporation to obtain a stronger article. However, it does serve for the manufacture of fertilizers; and since the contact process will eventually serve for the manufacture of all sulfuric acid, there appears little need for considering purification and concentration further. [For developments up to 1929 and 1932, see Spangler, *Ind. Eng. Chem.*, **21,** 417 (1929); Cobleigh, *Ind. Eng. Chem.*, **24,** 717 (1932). For a more detailed treatment of the lead-chamber process, see Abegg, Auerbach, and Koppel, *Handbuch der Anorganischen Chemie*, Hirzel, Leipzig, 1927, Vol. IV, part 1, p. 417.]

Sulfuric acid

Pure 100% sulfuric acid, H_2SO_4, is a colorless liquid whose melting point is 10.31°. When the liquid is heated, it gives off SO_3 and begins to boil at 290°, but the boiling temperature increases rapidly until it reaches 317°; at this point the liquid contains 98.54% H_2SO_4. The following table presents the temperatures at which sulfuric acid of various concentrations begins to boil; if boiling continues, the composition of the liquid changes and with it the boiling temperature [Knietsch, *Ber.*, **34,** 4106 (1901)].

TABLE 92

INITIAL BOILING POINTS OF SULFURIC ACID SOLUTIONS AND OLEUM

Pressure = 750–759 mm

(All concentrations are expressed in terms of SO_3 content. 100% H_2SO_4 contains 81.6% SO_3.)

Weight Per Cent SO_3	Boiling Point (°C)	Weight Per Cent SO_3	Boiling Point (°C)
50.36	140	82 3	212
57.88	162	83.4	170
66 44	202	86.45	125
72.84	240	89.5	92
78.56	292	93.24	60
80.44	317	99.5	43
81.56	273	—	—

Dilute solutions of sulfuric acid will become more concentrated, and the SO_3 content of oleum will decrease as boiling continues; the constant boiling mixture contains 98.5% H_2SO_4 (80.4% SO_3) and boils at 317° [326°, according to Lewis and Randall, *Thermodynamics*, p. 554].

The vapors of 100% sulfuric acid consist of H_2SO_4 at ordinary and moderate temperatures, but at about 300° dissociation into SO_3 and H_2O becomes measurable. Bodenstein and Katayama [*Z. phys. Chem.*, **69,** 26 (1909)] have determined the equilibrium constants for the reaction

$$H_2SO_4(g) = SO_3(g) + H_2O(g)$$

over the temperature range 325° to 483° and have expressed their results by means of the empirical equation,

$$\log_{10} K = -\frac{22850}{4.571T} + 0.75 \log_{10} T - 0.00057T + 4.086$$

$$K = \frac{(H_2O)(SO_3)}{(H_2SO_4)} \qquad \text{(Units are moles of vapor per liter.)}$$

At atmospheric pressure and 350°, the dissociation of 100% H_2SO_4 is 50%.

TABLE 93
THE PHYSICAL PROPERTIES OF SULFURIC ACID AND ITS HYDRATES
(0°C = 298.1°K)

Hydrate	Melting Point (°C)	Heat of Fusion (cal/mole)	Entropy of Liquid, 298.1°K (cal/deg/mole)	Heat Capacity in cal/deg/mole						
				Temperature (°K):						
				200	220	240	260	280	290	300
$H_2S_2O_7$	36									
H_2SO_4	10.31	2561	37.56	17.66(s)	19.02	20.29	21.47	22.66	32.33(l)	32.75
$H_2SO_4 \cdot H_2O$	8.47	4630	50.13	22.22(s)	23.98	25.79	27.62	29.45	50.54(l)	50.66
$H_2SO_4 \cdot 2H_2O$	−39.46	4379	66.15	27.27(s)	29.32	59.45(l)	60.34	60.97		61.45
$H_2SO_4 \cdot 4H_2O$	−28.25	7360	99.48	39.58(s)	43.00	46.51	91.47(l)	91.71		91.71

Free Energy of Hydration from Vapor-Pressure Data

$$H_2SO_4 \cdot H_2O + H_2O = H_2SO_4 \cdot 2H_2O$$

$$\Delta F^\circ_{298.1} = -2884 \text{ cal}$$

$$H_2SO_4 \cdot 2H_2O + 2H_2O = H_2SO_4 \cdot 4H_2O$$

$$\Delta F^\circ_{298.1} = -3535 \text{ cal}$$

In the system $SO_3—H_2O$, the following five hydrates have been observed [Pfanndler and Schnegg, *Wien. Ber.*, **71,** 351 (1875); Pickering, *J. Chem. Soc.*, **57,** 331 (1890); Knietsch, *Ber.*, **34,** 4106 (1901); Giran, *Compt. rend.*, **157,** 221 (1913); T. R. Rubin, *J. Am. Chem. Soc.*, to be published; Brönsted, *Z. phys. Chem.*, **68,** 693 (1910); Hülsman and Biltz, *Z. anorg. Chem.*, **218,** 369 (1934)]:

Hydrate	Melting Point (°C)
$H_2S_2O_7$	36
H_2SO_4	10.31
$H_2SO_4 \cdot H_2O$	8.47
$H_2SO_4 \cdot 2H_2O$	−39.46
$H_2SO_4 \cdot 4H_2O$	−28.25

The physical properties of sulfuric acid are given in Table 93; the complete phase diagram is shown in Fig. 66. A solution containing 36.5%

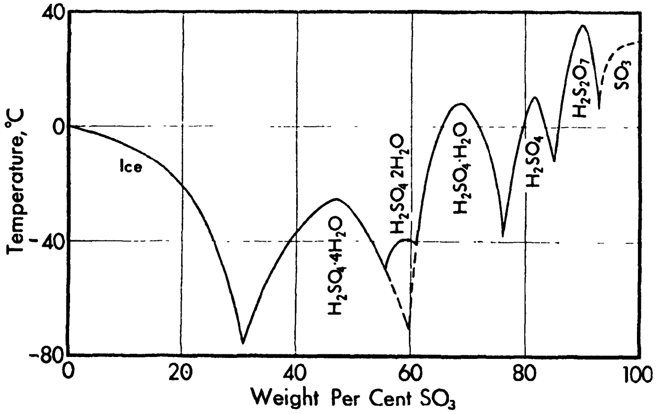

Fig. 66. Phase Diagram for the System $H_2O—SO_3$.

H_2SO_4 forms a eutectic mixture melting at −72.4°, the solid phases being $H_2O(s)$ and $H_2SO_4 \cdot 4H_2O$; Hülsman reports the octahydrate as existing in this mixture. The compound $H_2S_2O_7$ is known as pyrosulfuric acid; its salts are formed by heating certain bisulfates, for example, $KHSO_4$, but both the salts and the free acid hydrolyze rapidly in water to form sulfate and bisulfate ions and sulfuric acid. They differ in this behavior from the pyrophosphates, which hydrolyze slowly in water.

Other physical properties of sulfuric acid are shown graphically in Figs. 67, 68, and 69.

Aqueous sulfuric acid is a dibasic acid which ionizes to a different extent in the two steps

$$H_2SO_4 = H^+ + HSO_4^-$$

and

$$HSO_4^- = H^+ + SO_4^{=}$$

As a result of the comparative weakness of the second ionization, both the normal and the acid salts of sulfuric acid form. At concentrations up to 0.05 formal, the first step in the ionization may be assumed complete. The bisulfate ion does not ionize completely, as the values of the ionization constants in the following table show [Sherrill and Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926)]. The values of both

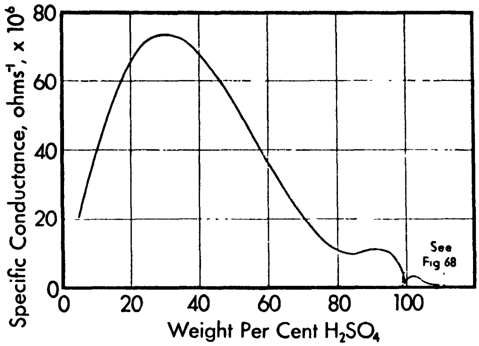

Fig. 67. The Specific Conductance of Sulfuric Acid Solutions at 18°C.

$$P = \frac{(H^+)(SO_4^{=})}{(HSO_4^-)} \quad \text{and} \quad K = \frac{\alpha_H \times \alpha_{SO_4^{=}}}{\alpha_{HSO_4^-}},$$

where (ion) represents the concentration of the ion in question and α its activity, are included in the table to show the effect of activity in an ionization reaction which is extensive (52-67%) and which involves doubly charged ions.

Table 94

THE IONIZATION CONSTANT OF BISULFATE ION IN SULFURIC ACID SOLUTIONS AT 25°

H_2SO_4 (moles/1000 g H_2O)	$P \times 10^2$	$K \times 10^2$
0.00025	1.18	1.05
.001	1.3	1.05
.005	1.68	1.12
.00625	1.75	1.13
.0125	2.08	1.19
.025	2.60	1.30
.050	3.52	1.48

$K = 1.15 \times 10^{-2}$ is best value.

It is evident that P varies considerably, while K is as constant as could be expected when the experimental data (conductance and transference numbers) for such dilute solutions are considered.

For higher concentrations of sulfuric acid, any calculations of a thermodynamic nature must make use of a table of experimentally determined activity coefficients. The following were determined by Harned and Hamer [*J. Am. Chem. Soc.*, **57**, 27 (1935)] from careful electromotive-force measurements in the range 0.001 m to 4.0 m and by Shankman and Gordon [*J. Am. Chem. Soc.*, **61**, 2370 (1939)] from accurate vapor-pressure measurements in the range 4.0 m to 16.0 m. In the latter range, electromotive-force measurements give results deviating somewhat from the vapor-pressure values, but the latter are considered more reliable. The values above 16.0 m were calculated by Dr. T. R. Rubin from the vapor-pressure data given by Collins [*J. Phys. Chem.*, **37**, 1191 (1933)] and by the International Critical Tables [Vol. 3, p. 303]; owing to the low accuracy of the data, these calculations are to be considered as useful approximations only. For purposes of comparison, the activity coefficients of sodium, magne-

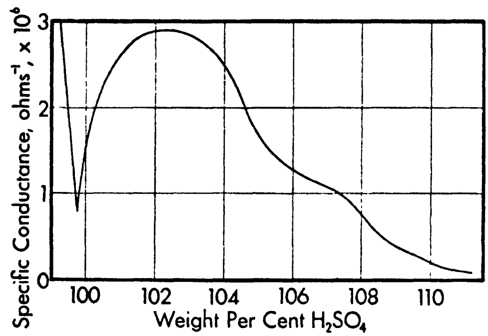

Fig. 68. The Specific Conductance of Sulfuric Acid Solutions at 18°C.

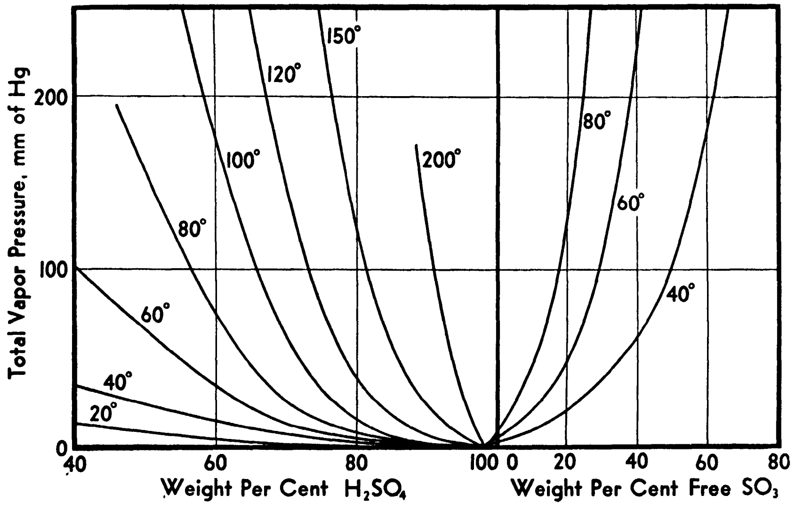

Fig. 69. The Vapor Pressure-Temperature-Composition Diagram for the System SO_3—H_2O. Temperatures are °C.

sium, and zinc sulfates are included in the table [Harned and Hecker, *J. Am. Chem. Soc.*, **56,** 650 (1934); Robinson and Jones, *ibid.*, **58,** 961 (1936); Randall and Scott, *ibid.*, **49,** 647 (1927)]. It will be noted that a minimum value of the activity coefficient γ for sulfuric acid is reached at about 2 m; the minimum value of γ for hydrochloric acid comes at about 0.5 m.

TABLE 95

ACTIVITY COEFFICIENTS OF SULFURIC ACID AND SOME OF ITS SALTS

Concentration (moles/1000 g H_2O)	Activity Coefficient			
	H_2SO_4	Na_2SO_4	$MgSO_4$	$ZnSO_4$
0.001	0.830	0.887	—	0.70
.002	.757	.847	—	.61
.005	.639	.778	—	.48
.01	.544	.714	0.40	.39
.02	.453	.641	.32	—
.05	.340	.53	.22	—
.1	.265	.45	.18	.15
.2	.209	.36	.13	.11
.5	.154	.27	.088	.065
1.0	.130	.20	.064	.045
2.0	.124	—	.055	.064
3.0	.141	—	.036	.04
4.0	.171			
6.0	.254			
8.0	.385			
10.0	.557			
12.0	.763			
14.0	1.008			
16.0	1.288			
20.0	1.97			
24.0	2.82			
28.0	3.71			
32.0	4.38			
36.0	5.09			
40.0	5.51			
45.0	5.96			
50.0	6.25			
55.0	6.47			

Sulfurous acid is readily oxidized to dilute sulfuric acid by even weak oxidizing agents, as the following free-energy equations show:

$$H_2SO_3 + I_3^- + H_2O = 4H^+ + SO_4^= + 3I^- \qquad \Delta F^\circ_{298} = -15{,}584 \text{ cal}$$
$$H_2SO_3 + Br_3^- + H_2O = 4H^+ + SO_4^= + 3Br^- \qquad \Delta F^\circ_{298} = -39{,}339$$
$$H_2SO_3 + Cl_2(aq) + H_2O = 4H^+ + SO_4^= + 2Cl^- \qquad \Delta F^\circ_{298} = -55{,}165$$
$$H_2SO_3 + 2Fe^{+++} + H_2O = 4H^+ + SO_4^= + 2Fe^{++} \qquad \Delta F^\circ_{298} = -26{,}435$$
$$H_2SO_3 + \tfrac{1}{2}O_2(g) = 2H^+ + SO_4^= \qquad \Delta F^\circ_{298} = -47{,}565$$

But it is well known that the first, second, and fourth reactions go to the left in concentrated sulfuric acid; consequently, the activity coefficients of both concentrated sulfuric acid and the two halogen acids in it must be very large indeed. Concentrated sulfuric acid may not be used in the distillation of hydrobromic and hydroiodic acids from their salts.

Sulfuric acid forms salts with most metals; the following table shows the solubilities of a number of typical sulfates in water at 25°.

TABLE 96

SOLUBILITIES OF SOME SULFATES IN WATER AT 25°

(The solubility *S* is in grams of anhydrous salt per 100 grams of water. Formulas are those of solid phases in equilibrium with the saturated solution.)

Salt	*S*	Salt	*S*	Salt	*S*
$Li_2SO_4 \cdot H_2O$	34.75	$CuSO_4 \cdot 5H_2O$	22.68	$MgSO_4 \cdot 7H_2O$	36.4
$Na_2SO_4 \cdot 10H_2O$*	28.0	Ag_2SO_4	8344	$ZnSO_4 \cdot 7H_2O$	57.45
K_2SO_4	12.04	$CaSO_4 \cdot 2H_2O$	.2086	$CdSO_4 \cdot \frac{8}{3}H_2O$†	76.79
$KHSO_4$	51.5	$SrSO_4$	.0134	Hg_2SO_4	
Rb_2SO_4	50.9	$BaSO_4$	.000223	Tl_2SO_4	5.459 (100 cc soln.)
Cs_2SO_4	181.4	$RaSO_4$	.00021 (20°)	$La_2(SO_4)_3 \cdot 9H_2O$	2.546

* At 32.38° (International Temp. Scale) the decahydrate is in equilibrium with the anhydrous salt and a saturated solution (Transition Temperature).

† The solubility of $CdSO_4 \cdot \frac{8}{3}H_2O$ varies but little with the temperature; thus, at 0° $S = 75.51$ g/100 g H_2O.

Because of the importance of sulfuric acid and the sulfates, reliable values for their free energies have been determined; in Table 97 are presented the free energies of formation of sulfuric acid and its ions, along with values for other common oxyacids of sulfur [Latimer, *Oxidation Potentials*].

TABLE 97

FREE ENERGIES OF FORMATION OF SULFUR ACIDS AND IONS AT 25°

(ΔF°_{298} [cal/mole])

$SO_2(g)$	−71,735	$SO_4^=$	−176,100
H_2SO_3	−128,535	$S_2O_8^=$	−257,000
HSO_3^-	−125,905	$H_2S(aq)$	−6,520
$SO_3^=$	−116,400	HS^-	2,950
$S_2O_4^=$	−143,400	$S^=$	23,420
$HS_2O_4^-$	−133,300	$H_2O(l)$	−56,690
$S_2O_6^=$	−248,000	OH^-	−37,585
$S_2O_3^=$	−124,000		

Selenic acid

Selenic acid, H_2SeO_4, may be prepared simply by dissolving SeO_3 in water, but since the preparation of the trioxide has so far been effected only in a low-pressure electric discharge (O_2 + Se), the simple method for preparing the acid is not yet a practical one. A common method for the preparation makes use of one or the other of the two following reversible reactions [Sherrill and Izard, *J. Am. Chem. Soc.*, **50,** 1665 (1928)]:

$$Br_2 + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Br^-$$

$$K = \frac{(H^+)^3(HSeO_4^-)(Br^-)^2}{(Br_2)(H_2SeO_3)} = 0.88 \text{ at } 25°$$

$$Cl_2 + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Cl^-$$

$$K = 1.42 \times 10^9 \text{ at } 25°$$

The equilibrium constants are expressed in terms of activities. Both reactions are slow, about one week being required to reach equilibrium with the chlorine reaction and two months with the bromine reaction. For preparative purposes it is desirable to have the reactions go to completion and eventually to be free of halogen. This is accomplished by the addition of silver oxide, Ag_2O, to the reaction mixture or, better still, by treating a suspension of Ag_2SeO_3 with aqueous bromine [Dennis and Koller, *J. Am. Chem. Soc.*, **41,** 949 (1919)]. The net reaction is then

$$Ag_2SeO_3(s) + Br_2 + H_2O = H_2SeO_4 + 2AgBr(s)$$

which goes practically completely to the right. Excess bromine is removed by passing air through the warmed solution, and the silver bromide can be filtered off, preferably with an asbestos or sintered glass filter. Any unoxidized selenious acid may be removed by treating the solution with hydrogen sulfide and then filtering. The resulting pure solution of H_2SeO_4 may be concentrated by evaporation, the acid itself being, like sulfuric acid, relatively involatile; but when heated above 210°, the concentrated acid (89%) decomposes into selenious acid and oxygen. It is better, indeed, not to evaporate the solution at much above 150°; the acid then contains about 80% selenic acid.

A second useful method of preparation is that of Meyer and Moldenhauer [*Z. anorg. Chem.*, **116,** 193 (1921)], in which selenious acid is oxidized with chloric acid, $HClO_3$, at the temperature of a water bath. The chloric acid is added in small portions until the oxidation is complete, and, after filtering through asbestos, the solution is freed from chlorine compounds by heating to 160–170°. The yield is from 90 to 95%. An electrolytic method of preparation has also been described [Manchot and Wirzmuller, *Z. anorg. Chem.*, **140,** 47 (1924)].

Still a third method of preparation is to be recommended in view of the present-day cheapness of the reagents used. Selenium dioxide (150 g) is added to 30% hydrogen peroxide (500 g) and the solution is allowed to stand 24 hours; the mixture is then refluxed in an all-glass apparatus for 12 hours. Additional hydrogen peroxide and further refluxing may be necessary for a complete reaction. The resulting solution is evaporated under reduced pressure on a steam bath, and finally dried air at 4–6 mm pressure is passed through the acid at 150–160° to remove the last traces of moisture. The product contains about 99% H_2SeO_4[McCrosky and Huff, *J. Am. Chem. Soc.*, **51**, 1457 (1929); Gilbertson and King, *ibid.*, **58**, 180 (1936)].

The most concentrated solutions obtainable by evaporation under a vacuum contain about 99% H_2SeO_4. The pure H_2SeO_4 is obtained by crystallization at room temperature, a "seed," prepared by freezing a small portion in solid carbon dioxide, being necessary to start crystallization [Macallan and Cameron, *Chem. News*, **59**, 207 (1889)].

Selenic acid forms two hydrates, $H_2SeO_4 \cdot H_2O$ and $H_2SeO_4 \cdot 4H_2O$, whose melting points are as follows:

	H_2SeO_4	$H_2SeO_4 \cdot H_2O$	$H_2SeO_4 \cdot 4H_2O$
m.p. (°C)	58	26	−51.7

The same hydrates are known for sulfuric acid, but it forms additional ones as well.

Aqueous solutions of selenic acid resemble, in their physical properties, those of sulfuric acid. Concentrated selenic acid is viscous, quite dense, and has a strong affinity for water. At 100° the vapor pressure of pure H_2SeO_4 is 15.8 mm; at 140°, 28.3 mm; and at 210°, 37.0 mm. If a dilute solution is evaporated at atmospheric pressure until the temperature reaches 205°, only water is given off and the composition of the residue corresponds to the monohydrate, $H_2SeO_4 \cdot H_2O$. In the accompanying table are presented the specific gravities of both selenic and sulfuric acid for a large range of concentrations for purposes of comparison [Diemer and Lehner, *J. Phys. Chem.*, **13**, 505 (1909)].

TABLE 98

THE SPECIFIC GRAVITIES, 20°/4°, OF SULFURIC AND SELENIC ACIDS

Per Cent H_2SO_4	Sp. Gr., 20°/4°	Per Cent H_2SeO_4	Sp. Gr., 20°/4°
4	1.0250	3.62	1.025
10	1.0661	9.82	1.075
19	1.1318	18.44	1.150
29	1.2104	28.58	1.250
37	1.2769	37.34	1.350
53	1.4249	52.98	1.550
66	1.5646	65.90	1.800
79	1.7159	79.28	2.100
90	1.8144	90.10	2.400
95	1.8337	94.64	2.500
99	1.8342	99.04	2.590

Aqueous selenic acid, like sulfuric acid, ionizes in two steps. At low concentrations the ionization of the first hydrogen is complete.

$$H_2SeO_4 = H^+ + HSeO_4^-$$

But the second hydrogen comes off with greater difficulty [Sherrill and Lyons, *J. Am. Chem. Soc.*, **54,** 979 (1932)],

$$HSeO_4^- = H^+ + SeO_4^=$$

$$K = \frac{(H^+)(SeO_4^=)}{(HSeO_4^-)} = 1.15 \times 10^{-2} \text{ at } 25°$$

the equilibrium constant here being expressed in terms of activities. In a 0.01 m solution of H_2SeO_4, the $HSeO_4^-$ is about 67% and in a 0.1 m solution 25% ionized. The ionization constant for the biselenate ion is the same as that for bisulfate ion. That the two acids are nearly identical in their ionizing properties was shown by Sherrill and Lyons, who found the emf of the cells *Pt, Quinhydrone* H_2SO_4 (*C formal*), H_2SeO_4 (*C formal*) *Quinhydrone, Pt,* to be essentially zero over the concentration range $C = 0.0100$ to 0.8000 formal.

Selenic acid solutions are more rapidly reduced than are those of sulfuric acid. The 0.8% acid does not oxidize iodide ion, but more concentrated solutions react slowly with it with the formation of iodine and elementary (red) selenium. With selenic acid of moderate to high concentrations, hydrobromic and hydrochloric acids react slowly and reversibly to form the elementary halogen and selenious acid. Sulfurous acid reacts slowly with H_2SeO_4 to give elementary selenium and sulfuric acid. When dilute H_2SeO_4 in hydrochloric acid is treated with hydrazine at 60°, elementary selenium is quantitatively precipitated [Dennis and Koller, *J. Am. Chem. Soc.*, **41,** 949 (1919)].

A still clearer and more quantitative expression for the oxidizing power of selenic acid is provided by the following molal free energies of formation; the values for the corresponding sulfur acids are included for the sake of comparison [Latimer, *Oxidation Potentials*]. The difference between the ΔF°_{298} for a selenate and that for a selenite is much smaller than the corresponding difference for a sulfate and sulfite, and, consequently, selenates are much stronger oxidizing agents than are the sulfates.

	ΔF°_{298}		ΔF°_{298}
$HSeO_4^-$	−107,840	H_2SeO_3	−101,361
HSO_4^-	−178,820	H_2SO_3	−128,535
$SeO_4^=$	−105,120	$HS_2O_3^-$	− 97,850
$SO_4^=$	−176,100	$SeO_3^=$	− 87,890
		$SO_3^=$	−116,400

Selenic acid forms normal and acid salts whose properties frequently bear a close resemblance to the corresponding sulfates. For example, the salt $Na_2SeO_4 \cdot 10H_2O$ undergoes a transition to Na_2SeO_4 at 30.3°; the corresponding transition between $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4 takes place at 32.38°. The following solubilities, S, in grams of the anhydrous salt per 100 grams of water at 25°, of both selenates and sulfates show the similarities and the differences of the salts formed. The formulas indicate the solid phase in each case. It is evident that the selenates and sulfates of the same element are quite similar; in most cases the crystals are isomorphous [see the many papers by Tutton on the subject in *J. Chem. Soc.* and *Proc. Roy. Soc.*]. The selenates are more soluble in water than are the corresponding sulfates.

TABLE 99
SOLUBILITIES OF SELENATES AND SULFATES AT 25°

	S		S
$CaSeO_4 \cdot 2H_2O$........	7.39	$CaSO_4 \cdot 2H_2O$........	0.2086
$BaSeO_4$.............	.008	$BaSO_4$	.000223
$MgSeO_4 \cdot 7H_2O$*......	29.87 (8°)	$MgSO_4 \cdot 7H_2O$.......	36.4
$Na_2SeO_4 \cdot 10H_2O$.....	57.88	$Na_2SO_4 \cdot 10H_2O$	28.0
K_2SeO_4.............	112.09	K_2SO_4.............	12.04
Rb_2SeO_4............	158.9	Rb_2SO_4............	50 9
$CuSeO_4 \cdot 5H_2O$..	43	$CuSO_4 \cdot 5H_2O$.......	22.68

* At 25° the hexahydrate is the solid phase; $S = 37.93$ g/100 g H_2O.

The structure of the sulfate and selenate ions in crystals of their salts is tetrahedral; the sulfur or selenium atom occupies the center and the four oxygen atoms the corners of a regular tetrahedron. The approximate interatomic distance S—O is 1.51 Å and Se—O is 1.61 Å as estimated from the results of X-ray crystal-structure studies made on a number of sulfates and selenates.

Fluosulfonic, chlorsulfonic, and chlorselenic acids, HSO_3F, HSO_3Cl, and $HSeO_3Cl$

Fluosulfonic acid is prepared either by the action of concentrated hydrofluoric acid on sulfur trioxide or, usually more conveniently and very nearly quantitatively, by distilling it from a mixture of calcium fluoride and fuming sulfuric acid (60% SO_3) in an iron vessel [Ruff, *Ber.*, **47**, 652 (1914); Traube and Lange, *Ber.*, **57**, 1038 (1924)]. It is also a by-product in the preparation of anhydrous hydrogen fluoride from CaF_2 and ordinary concentrated sulfuric acid. Meyer and Schramm [*Z. anorg. Chem.*, **206**, 24 (1932)] prepared the acid by adding KHF_2, (20 g) slowly and with stirring, to well-cooled (ice-salt) fuming sulfuric acid (40 cc) in a platinum dish. After heating the resulting viscous mass slowly to 100° to volatilize any excess SO_3 and HF, it is transferred to a glass vessel and distilled until the temperature reaches 250°; the distillate consists of nearly pure fluosulfonic acid.

Fluosulfonic acid is a colorless liquid with a disagreeable odor; it boils at 162.6° and its freezing point is not known. The acid does not attack glass or most of the common metals at ordinary temperatures. Mercury is oxidized slowly and organic materials (cork, wood, and rubber) are charred by HSO_3F. There is no tendency toward decomposition of the vapors of HSO_3F even at 900°. When fluosulfonic acid is dissolved in water, a slow hydrolysis takes place according to the equation,

$$HSO_3F + H_2O = H_2SO_4 + HF$$

and this reaction is reversible, as is witnessed by the fact that concentrated H_2SO_4 and HF react to give fluosulfonic acid. In dilute aqueous solution the hydrolysis, at equilibrium, is practically complete. No investigations of the rate of hydrolysis have been made, but the equilibrium has been studied [Lange, *Z. anorg. Chem.*, **215**, 321 (1933)]. Because the equilibrium mixture is not simple, that is, because the activities of the H_2SO_4, HF, HSO_3F, and H_2O in the concentrated acid mixture are not known, the evaluation of true equilibrium constants has not been attained; the mass action function reported by Lange for 24° probably has little relation to the true equilibrium constant.

Salts of fluosulfonic acid may be prepared by adding the fluoride to sulfur trioxide or fuming sulfuric acid. Thus if dry ammonium fluoride, NH_4F, (65 g) is gradually dissolved in 150 g of cooled (0°) fuming sulfuric acid (79% SO_3) in an enameled iron vessel, a vigorous reaction takes place and a pasty mass results. This mass is treated with ammoniacal methyl alcohol, which dissolves most of the ammonium fluosulfonate but not ammonium fluoride or sulfate. The alcoholic solution is then evaporated to obtain the colorless crystals of ammonium fluosulfonate, NH_4SO_3F, m.p. 245°. If this ammonium salt is distilled with concentrated sulfuric acid, the distillate consists of fluosulfonic acid. Ammonium fluosulfonate dissolves readily in water without appreciable hydrolysis even after long standing [Traube, Hoerenz, and Wunderlich, *Ber.*, **52**, 1272 (1919)]. It may be used as the starting material for the preparation of other salts; for example, $LiSO_3F \cdot 3H_2O$ (m.p. 61°) may be crystallized as long, shining needles from an aqueous mixture of LiOH and NH_4SO_3F. For the most part the fluosulfonates are readily soluble in water ($CsSO_3F$, 2.23 g/100 cc soln. at 0°), but nitron fluosulfonate is so sparingly soluble that it may be made the basis for a gravimetric method of analysis. Some of the fluosulfonates, notably $Ba(SO_3F)_2$, decompose on heating to give SO_2F_2. A number of more complex salts have been prepared by Wilke-Dörfurt, Balz, and Weinhardt [*Z. anorg. Chem.*, **185**, 417 (1930)].

Chlorsulfonic acid, HSO_3Cl, may be prepared by reacting dry hydrogen chloride directly with sulfur trioxide or with fuming sulfuric acid (70% SO_3) [Sanger and Riegel, *Z. anorg. Chem.*, **76**, 79 (1912)]. It may also be obtained by adding sodium chloride (1 mole) to fuming sulfuric acid (H_2SO_4 (1 mole) + SO_3 (2 mole)). A number of other chlorides, for example, PCl_3, PCl_5, $POCl_3$, and CCl_4, react with fuming sulfuric acid to form chlorsulfonic acid. In all of these methods of preparation, the chlorsulfonic acid is distilled from the reaction mixture as a colorless, fuming liquid having a very disagreeable odor. Liquid chlorsulfonic acid boils, with some decomposition into HCl and SO_3, at 152°, and the solid melts at about −80°; the density of the acid is 1.753 at 20°.

That the reaction $SO_3(g) + HCl(g) = HSO_3Cl(g)$ is reversible there is no reason to doubt, but owing to its slowness and complications arising out of side reactions, such as the formation of SO_2, Cl_2, H_2O, or even SO_2Cl_2, no reliable measurements of the equilibrium have been made [see, *e.g.*, Sanger and Riegel, *loc. cit.*]. At 184° the vapor density of HSO_3Cl is 2.4 compared with air as unity, while the calculated value, assuming no dissociation, is 4.04.

Chlorsulfonic acid reacts readily with water to form a solution of sulfuric and hydrochloric acid; the reaction is rapid, in contrast with the corresponding hydrolysis of fluosulfonic acid. Since HSO_3Cl fumes in air, it has found application as a smoke-producer in military operations, although here a mixture of sulfur trioxide and HSO_3Cl (sp. gr. 1.91, m.p. −30°) has been found more effective for the purpose [Prentiss, *Chemicals In War*, p. 238]. The most useful applications of HSO_3Cl are in organic chemistry, where it serves as a valuable sulfonating agent. Salts of chlorsulfonic acid have been prepared, notably $NaSO_3Cl$, by the addition to it of a dry chloride; the sodium salt reacts with pyrosulfuric acid to form HSO_3Cl and sodium pyrosulfate. With water $NaSO_3Cl$ hydrolyzes rapidly to form sodium, hydrogen, sulfate, and chloride ions.

When fuming sulfuric acid is refluxed with carbon tetrachloride over a water bath, the following reaction takes place:

$$2SO_3 + CCl_4 = COCl_2 + S_2O_5Cl_2$$

and the yield of the pyrosulfuryl chloride, $S_2O_5Cl_2$, varies from zero, if pure H_2SO_4 is used, to 31.5% with $H_2S_2O_7$ and to 100% with SO_3 alone. After the reaction is complete (Note: Phosgene is formed. Danger), the mixture is distilled and the middle fraction coming off at 130–160° is collected and further fractionated; the portion coming off above 130° contains most of the $S_2O_5Cl_2$. In order to remove any HSO_3Cl, the $S_2O_5Cl_2$-rich fraction is treated with dry NaCl.

$$HSO_3Cl + NaCl = NaSO_3Cl + HCl$$

The resulting mixture is warmed to expel the HCl, and it is then distilled to obtain the $S_2O_5Cl_2$ as the distillate. Pyrosulfuryl chloride, the anhydride of HSO_3Cl, is a colorless, mobile liquid boiling at 152° and having a density of 1.872 at 0°. The melting point of the solid is −37°. The vapors are quite stable toward decomposition, as is shown by the fact that the average vapor density at 184° is 7.4 (air unity), which is in accord with the calculated value 7.49 [Sanger and Riegel, *Z. anorg. Chem.*, **76,** 79 (1912)]. At higher temperatures a somewhat complicated decomposition doubtless takes place. The heat of vaporization of the liquid is 7550 cal/mole. Liquid $S_2O_5Cl_2$ fumes slightly, if at all, in air, and it reacts only slowly with water but readily with aqueous alkali to form sulfate and chloride ions. It reacts slowly with Au, Pt, and Hg (above 60°) and more rapidly with the less noble metals to form the chlorides. With organic substances it acts as a chlorinating agent.

No attempt to prepare fluoselenic acid appears to have been made. Chlorselenic acid, $HSeO_3Cl$, has been reported by Worsley and Baker [*J. Chem. Soc.*, **123,** 2870 (1923)] as resulting from the action of HCl on SeO_3 (O_3 + Se (in $SeOCl_2$)) at 0°. It is described as a nearly colorless, fuming liquid having a density of 2.26 and freezing at −46°. It decomposes slowly at room temperature to form Se, SeO_2, and HCl (and, presumably, O_2 or Cl_2); on heating, the decomposition is more rapid. It dissolves in water (H_2SeO_4 + HCl) with the evolution of considerable heat, but does not react with ether, benzene, chloroform, or CCl_4.

Telluric acid, H_6TeO_6

Probably the simplest method for the preparation of telluric acid is that of Gilbertson [*J. Am. Chem. Soc.*, **55,** 1460 (1933)], in which metallic tellurium or tellurium dioxide is refluxed with a mixture of 30% hydrogen peroxide (two volumes) and concentrated sulfuric acid (one volume) until all of the metal or the dioxide has dissolved and active effervescence has ceased. The resulting solution is filtered through asbestos, and the filtrate is evaporated until crystals just begin to appear. Concentrated nitric acid is then added to bring down the colorless crystals of orthotelluric acid, H_6TeO_6. After filtering the resulting mixture through asbestos, the crystals are heated sufficiently to drive off any adhering nitric acid and are then recrystallized from their hot solution in water.

In order to indicate the strength of the oxidizing agents necessary to convert TeO_2 into telluric acid, two further methods for the preparation of H_6TeO_6 may be described only briefly. Boiling nitric acid solutions of TeO_2 may be oxidized to H_6TeO_6 by the slow addition of just the right amount of chromium trioxide, CrO_3 [Standenmaier, *Z. anorg. Chem.*, **10,** 218 (1895)]. When a hot hydrochloric acid solution of tetravalent tellurium is treated with chloric acid, $HClO_3$, the oxidation to telluric acid is effected [Meyer and Moldenhauer, *Z. anorg. Chem.*, **119,** 132 (1921)].

In both of these methods the H_6TeO_6 is eventually crystallized from an aqueous solution and then purified by recrystallization.

Orthotelluric acid in the solid state is usually obtained as fine, snow-white crystals consisting of H_6TeO_6, if the crystallization from water is carried out above 10°, and of $H_6TeO_6 \cdot 4H_2O$ if crystallized below this temperature. The anhydrous acid exists in two allotropic modifications, the α or cubic form being obtained by crystallizing from concentrated nitric acid, and the thermodynamically stable (at room temperatures) β or monoclinic form by crystallization from water or dilute acid solutions. When heated, the cubic form goes over into the monoclinic, but the transition temperature, if one exists for atmospheric pressures, is not known.

When H_6TeO_6 is strongly heated, it loses water and is converted first into the so-called allotelluric acid, then into the yellowish TeO_3, and finally into TeO_2 and oxygen. If the acid is heated at 140° for 24 hours in a sealed tube, it melts to a light-yellow, sirupy, viscous liquid which, on cooling, is soluble in all proportions in water to give, at times, milky solutions. This acid is known as allotelluric acid and is believed to be complex and possibly not unlike the complex tungstic or molybdic acids; freezing-point experiments indicate three tellurium atoms per molecule. It is a stronger acid than H_6TeO_6, since its conductance is 28 times greater. The aqueous solutions hydrolyze slowly (two to three days) to orthotelluric acid, H_6TeO_6; in alkaline solutions the hydrolysis is rapid [Pascal and Patry, *Compt. rend.*, **200,** 708 (1935); Patry, *Compt. rend.*, **200,** 1597 (1935); *Bull. soc. chim.*, **3,** 845 (1936)].

The solubility of H_6TeO_6 and $H_6TeO_6 \cdot 4H_2O$ in water has been determined over the temperature range from 0° to 110° by Mylius [*Ber.*, **34,** 2208 (1901)], and his results, recalculated to a more rational basis, are presented in the following table.

TABLE 100

THE SOLUBILITY, *S*, OF ORTHOTELLURIC ACID IN WATER

(S is expressed in g of H_6TeO_6 per 100 g of water.)

$H_6TeO_6 \cdot 4H_2O$		H_6TeO_6	
Temperature (°C)	S (g/100 g H_2O)	Temperature (°C)	S (g/100 g H_2O)
0	19.9	10	42.9
5	27.0	30	65.7
10	45.2	60	104.5
15	64.1	80	158.0
		100	260.8
		110	386.5

Aqueous solutions of orthotelluric acid are only weakly ionized, as is shown by the following freezing-point and conductance data [Gutbier, *Z. anorg. Chem.*, **29,** 23 (1902); Rosenheim and Jander, *Koll. Z.*, **22,** 23 (1918)].

TABLE 101

FREEZING-POINT AND CONDUCTANCE DATA FOR ORTHOTELLURIC ACID

Formula weight = 229.66.

H_6TeO_6 (g/100 g H_2O)	$-\Delta T$ (°C)	Molecular Weight (calc.)	H_6TeO_6 (liters/mole)	Conductance (Ohm^{-1} $mole^{-1}$ at 25°)
1.610	0.140	218.5	4	0.1902
4.327	.385	213.8	8	.1984
2.288	.190	228.7	16	.2029
1.694	.160	201.4	32	.2119
			128	.2611
			513	.4460
			1024	.6913

It is evident from the freezing points that the ionization is small, although the experimental errors appear to be appreciable and do not permit of a reliable estimate of an ionization constant. The molal conductances are quite small and are a more accurate indication of the weakness of the acid. Attempts to determine the ionization constants by indicator methods have been made by Rosenheim and Janders and by Blanc [*J. chim. phys.*, **18,** 28 (1920)], but since their results are not in accord with each other, it is not certain which values are correct.

$$\left.\begin{aligned}\frac{(H^+)(H_5TeO_6^-)}{(H_6TeO_6)} = K_1 &= 6.8 \times 10^{-7}\\ K_2 &= 4.1 \times 10^{-11}\end{aligned}\right\}\ \text{(Blanc)}$$

$$K_1 = 1.6 \times 10^{-9} \quad \text{(Rosenheim and Janders)}$$

In Blanc's experiments, only two inflections were observed in the neutralization curve; this fact, together with the fact that the known alkali metal salts of orthotelluric acid have the forms MH_5TeO_6 and $M_2H_4TeO_6$, show the acid to be primarily dibasic. Experiments with the glass electrode might yield more satisfactory results for the ionization constants.

The structure of the cubic form of H_6TeO_6 as determined by X-ray methods is that of a regular octahedron with the tellurium atom at the center and six OH groups at the corners [Pauling, *Z. Krist.*, **91,** 367 (1935); Passerini and Rollier, *Atti. accad. Lincei.*, **21,** 364 (1935)]. This structure indicates the reason for the dibasic character of the acid, that is, that the nearness of the OH groups to each other inhibits more than two hydrogens from ionizing readily.

Telluric acid is a good oxidizing agent, as is shown by its oxidation potential

$$4H_2O + TeO_2(s) = H_6TeO_6(s) + 2H^+ + 2E^- \qquad E^\circ = -1.02 \text{ volts}$$

and by its action on other substances. Thus at 45°, chlorine is liberated from a concentrated hydrochloric acid solution, with the formation of TeO_2; both Te and TeO_2 result from mixing solutions of H_6TeO_6 and HI; and Te and Br_2 are formed when hydrobromic acid solutions of H_6TeO_6 are boiled. Hydrogen sulfide reduces H_6TeO_6 slowly even at 100° to tellurium sulfides (TeS_2 and TeS) and Te, and sulfurous acid reacts more slowly still with the formation of Te [Benger, *J. Am. Chem. Soc.*, **39,** 2179 (1917)]. When solutions of H_6TeO_6 are heated with Te, Se, or S, slow reduction to TeO_2 with the two former and to Te with the last results. Hydrazine or hydroxylamine in ammoniacal solution will reduce telluric acid quantitatively to elementary tellurium. Hot, and sometimes cold, solutions of telluric acid will attack the metals Ag, Hg, Pb, Bi, Cu, Zn, As, Sb, Sn, Al, Cd, and Ni. When an alkaline solution of a tellurate and a cupric salt is heated, a brown solution results which is a sensitive test for tellurium [Feigl and Uzel, *Mikrochem.*, **19,** 132 (1936)]. With a freshly prepared solution of $[Cr(NH_3)_6](NO_3)_3$, a hot ammoniacal tellurate solution produces a colored precipitate of $[Cr(NH_3)_6]_2(H_4TeO_6)_3$ with even 0.16 mg of tellurium in 10 cc of solution [Bersin, *Z. anal. Chem.*, **91,** 170 (1932)].

The salts of telluric acid differ considerably from those of sulfuric and selenic acids. When telluric acid solutions are treated with more than two equivalents of NaOH and then heated for a short time, colorless crystals of $Na_2H_4TeO_6$ are obtained that are soluble in water to the extent of 0.7 g/100 g soln. at 25° and 1.1 g/100 g soln. at 50°; these solubilities do not correspond, apparently, to an equilibrium condition, since they have not been found to be reproducible [Rosenheim and Jander, *Koll. Z.*, **22,** 23 (1918)]. The potassium salts $K_2H_4TeO_6$, $K_2H_4TeO_6{\cdot}3H_2O$, $K_2H_4TeO_6{\cdot}3\frac{1}{2}H_2O$, and $K_2H_4TeO_6{\cdot}5H_2O$ can be obtained by slowly evaporating a solution containing excess KOH; the evaporation is carried out in a desiccator containing sulfuric acid. The more common $K_2H_4TeO_6{\cdot}3H_2O$ is much more soluble, about 60 g/100 g H_2O at room temperature, than the sodium salt; the results of solubility experiments indicate that both the sodium and potassium salts undergo slow but marked changes when dissolved in water, since with an ultramicroscope colloidal particles are observed. Just what the composition of the solutions is, is not known. A silver salt, $Ag_2H_4TeO_6$, can be obtained as yellow crystals by allowing a mixture of aqueous silver nitrate and concentrated potassium tellurate containing a little free acetic acid to stand for several hours [Hutchins, *J. Am. Chem. Soc.*, **27,** 1157 (1905)]; exposure to light causes the crystals to darken. On evaporation of more dilute mixtures of silver nitrate and potassium tellurate (containing a little nitric acid), ruby red monoclinic crystals of another tellurate of silver, $Ag_3H_3TeO_6$, are formed. It is evident from the methods of preparation that neither of these silver salts is sparingly soluble in water, but the solubilities are not known. When solutions of mercurous nitrate and telluric acid are mixed, a bright-yellow precipitate forms which, in the presence of excess telluric acid, slowly changes to colorless triclinic crystals of $HgH_5TeO_6 \cdot H_2O$. The mercuric salts Hg_3TeO_6 (yellow, insoluble), $HgTeO_4$ (amorphous, white), and HgH_4TeO_6 (colorless) are known, and zinc forms Zn_3TeO_6 (colorless, insoluble). In general, the ortho acid tellurates are the most common, and neither they nor the other known tellurates are isomorphous with the corresponding selenates. Because telluric acid is weak, its salts are usually soluble in strong acids. Both the chemical and physical properties of telluric acid and its salts differ considerably from those of the selenates and sulfates.

Sulfoxylic, Dithionous, and Dithionic Acids

We come now to three oxyacids of sulfur that do not possess anhydrides and that structurally and chemically are different from the polythionic acids. Sulfoxylic acid, H_2SO_2, if it exists, may be looked upon as the simplest sulfone, of which there are many organic derivatives, and as a possible handy intermediate to use in explaining the complexities of Wackenroder's solution. Dithionous and dithionic acids, $H_2S_2O_4$ and $H_2S_2O_6$, are characterized, structurally, by the presence of two equivalent sulfur atoms bound together, and this sulfur-sulfur bond gives the compounds properties quite distinct from those exhibited by thiosulfates and the polythionates.

Sulfoxylic acid, H_2SO_2

Free sulfoxylic acid is not known, but two of its salts have been reported, namely, Na_2SO_2 and $ZnSO_2$. The former is described by Vogel and Partington [*J. Chem. Soc.*, **127**, 1514 (1925)] as resulting from the action of S_2O_3 (from $S + SO_3$) on sodium ethylate. The mixture is allowed to stand overnight and is then acidified with dilute sulfuric acid, whereupon a white crystalline precipitate of Na_2SO_2 comes down. The salt is relatively stable toward heating and is only moderately soluble in water; it is insoluble in alcohol. It is a strong reducing agent [see Bassett and Durant, *J. Chem. Soc.*, 1401 (1927), for a critique of the results of Vogel and Partington]. The zinc salt, $ZnSO_2$, is believed by Fromm and Palma [*Ber.*, **39**, 3317 (1906)] to have resulted from the reaction between zinc dust and an ether solution of sulfuryl chloride. Whether or not these salts of sulfoxylic acid have, in reality, been prepared is not certain, but the stable organic sulfones, R_2SO_2, are well known. For example, "mustard gas," $(ClC_2H_4)_2S$, is readily oxidized by hypochlorite to $(ClC_2H_4)_2SO_2$, a compound that resists further oxidation under ordinary conditions. Other organic sulfones, *e.g.*, $(C_2H_5)_2SO_2$, are such stable substances that they are hydrolyzed only by strong alkalis at somewhat elevated temperatures. Sulfoxylic acid is frequently *assumed* as an intermediate to explain some of the complicated reactions taking place in Wackenroder's solution.

Dithionous (hyposulfurous) acid, $H_2S_2O_4$

When an aqueous solution of sulfurous acid, H_2SO_3, is poured through a Jones reductor, the resulting mixture is yellowish in color, acts as a very strong reducing agent, and contains hyposulfurous acid. These solutions ordinarily contain some acid and are not very stable; they decompose according to the equation

$$2S_2O_4^{=} + H_2O = S_2O_3^{=} + 2HSO_3^{-}, \qquad \Delta F^\circ_{298} = -59{,}100 \text{ cal}$$

The rate of the reaction is increased if further acid is added; the presence of acid brings about the further decomposition of the thiosulfate to sulfite and sulfur, so that the over-all reaction becomes

$$S_2O_4^{=} + H_2O = H_2SO_3 + S$$

Solutions of the alkali metal salts of hyposulfurous acid decompose at a slow but measurable rate at ordinary temperatures (0–60°), but the free acid in aqueous solutions cannot exist for an appreciable length of time. On acidifying solutions of the salts, they become orange to orange-yellow in color, but there is some doubt whether the color is due to $H_2S_2O_4$ or to the elementary sulfur that is formed [Bassett and Durant, *J. Chem. Soc.*, 1401 (1927)]. Since the acid is so unstable, and since the sodium salt is of considerable importance, the discussion will be confined mainly to the latter substance.

Sodium hyposulfite is an article of commerce and is used as a reducing agent in the dye industry. It is prepared by stirring a solution of $NaHSO_3$ with zinc dust for about two hours at 30–40°. Milk of lime is then added and the mixture is filtered; the filtrate is warmed to 50–60° and an easily soluble sodium salt (NaCl, $NaNO_3$, $NaCH_3CO_2$, or NaOH) added to precipitate the sodium hyposulfite, $Na_2S_2O_4 \cdot 2H_2O$. The $Na_2S_2O_4 \cdot 2H_2O$ is filtered off and dried to the anhydrous salt by heating to 60–70° in a vacuum or by extracting with absolute alcohol. Oxygen must be excluded in all operations, and the solutions must be kept alkaline to prevent decomposition [see, *e.g.*, Badische Analin and Soda Fabrik patent, D.P. 148125 (1902); Jellinek, *Z. anorg. Chem.*, **70**, 93 (1911)]. The presence of a small amount of starch or gum in the dried salt acts to protect it to some extent from atmospheric oxidation. The alcohol-dried salt can be obtained nearly pure, the purity ranging from 96 to

98%; the commercial product is ordinarily about 80% pure. Reducing agents other than zinc have been used in the preparation; among these may be mentioned sodium amalgam, suspensions of metallic sodium in alcohol-ether mixtures, and zinc amalgam. Hyposulfites may also be prepared electrolytically [Jellinek, *Z. phys. Chem.*, **93,** 325 (1919)], but the process has not yet become of industrial importance.

Anhydrous sodium hyposulfite reacts much less rapidly with oxygen than does the dihydrate, and for this reason the former is the salt ordinarily manufactured. Aqueous solutions of $Na_2S_2O_4$ absorb oxygen very rapidly according to the reaction [Nicloux, *Compt. rend.*, **196,** 616 (1933)],

$$S_2O_4^= + O_2 + H_2O = HSO_4^- + HSO_3^-$$

and the dihydrate, $Na_2S_2O_4 \cdot 2H_2O$, is oxidized rapidly to pyrosulfite.

$$Na_2S_2O_4 \cdot 2H_2O + \tfrac{1}{2}O_2 = Na_2S_2O_5 + 2H_2O$$

The physical properties of sodium hyposulfite have received moderate attention. At 20° the solubility of $Na_2S_2O_4 \cdot 2H_2O$ is 21.8 g per 100 g of water; at 1°, 100 g of saturated solution contains 12.85 g of $Na_2S_2O_4$. At 52° both the dihydrate and the anhydrous salt are present in equilibrium with the solution, which contains 2.8 mole per cent of salt. There is an eutectic at −4.58° where solution, ice, and the dihydrate are present together.

Measurements of the freezing-point lowering show the true formula of the hyposulfite ion to be $S_2O_4^=$ [see Jellinek, *Z. anorg. Chem.*, **70,** 119 (1911)]. That the experimental values of the molecular weight are not constant and are less than the formula weight is probably due to imperfections of the solutions. The molal conductances were also measured by Jellinek, who found $\Lambda_\infty = 240$ at 25°.

$Na_2S_2O_4$ (g/100 g H_2O)	Freezing Temperature (°C)	Molecular Weight (calc.)
1.05	−0 28	139
3.19	− .84	140
5.04	−1.30	144
11.23	−2.66	156
17.67	−4.17	157
19.27	−4.48	159

Formula weight $Na_2S_2O_4$ = 174.

The ionization constants of $H_2S_2O_4$ were determined by Jellinek by the device of adding equivalent amounts of HCl to solutions of $Na_2S_2O_4$ and then measuring the conductance of the resulting mixture. The first hydrogen ionizes practically completely, and for the second

$$\frac{(H^+)(S_2O_4^=)}{(HS_2O_4^-)} = 3.5 \times 10^{-3} \text{ at } 25^\circ$$

It has been remarked that solutions of sodium hyposulfite decompose slowly according to the equation

$$2S_2O_4^= + H_2O = 2HSO_3^- + S_2O_3^=$$

The rate of this reaction was studied by Jellinek [*Z. phys. Chem.*, **93,** 325 (1919)] both in the absence and in the presence of added bisulfite. At 60°, solutions containing only $Na_2S_2O_4$ (5 g/100 g H_2O) decomposed according to a second-order rate equation:

$$-\frac{d(S_2O_4^=)}{dt} = k'(S_2O_4^=)^2$$

$$k' = 0.40 \text{ mole}^{-1} \text{ min}^{-1} \text{ at } 60^\circ$$

In the presence of added bisulfite ion, the rate of the decomposition could be measured at lower temperatures (0–32°), and under these conditions the rate equation takes the form:

$$-\frac{d(S_2O_4^=)}{dt} = k(S_2O_4^=)^2(HSO_3^-)^2$$

This relation suggests that the ion $HS_2O_4^-$ is the reactive species, but further analysis of Jellinek's results and additional experiments will be required before a satisfactory mechanism can be given.*

The hydrosulfites are noteworthy for their strength as reducing agents. An alkaline solution of Sb^{III}, Bi^{III}, or Pb^{II} containing some KCN will, on adding $Na_2S_2O_4$ and warming, precipitate the metals. Cupric copper is reduced to metallic copper, and solutions of Ag^{I} give metallic silver with hyposulfites. Iodine and iodate in neutral solution bring about oxidation to the sulfate stage, but permanganate produces some dithionate as well as sulfate. For analytical purposes, an excess of cupric ammonia sulfate solution is added to the hyposulfite; and after solution and reaction (rapid) are complete, the excess $Cu(NH_3)_4^{++}$ is titrated with standard $Na_2S_2O_4$ until the blue solution becomes colorless [Jellinek, *Z. anorg. Chem.*, **70,** 98 (1911)]. The reaction involved is:

$$2Cu(NH_3)_4^{++} + S_2O_4^= + 2H_2O = 2Cu^+ + 2SO_3^= + 4NH_4^+ + 4NH_3$$

Methylene blue may be used as an additional indicator in this method, since it is decolorized by hyposulfites. Knecht and Hibbert [*Ber.*, **40,**

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* Preliminary experiments by Mr. Malcolm Mason at the California Institute indicate that the reaction is first-order with respect to dithionite and to bisulfite and is independent of the sulfite ion concentration.

3819 (1907)] have devised an ingenious method of analysis in which an excess of standard methylene blue is added to the hyposulfite and the excess dye then determined with titanous chloride or sulfate. Still another analytical method depends on the reduction of ferricyanide to ferrocyanide, an outside indicator of Fe^{++} being used to determine the endpoint. Iodimetric methods for the estimation of hyposulfites have also been used.

In turn, sodium hyposulfite solutions may be used as analytical reducing agents; they may also be used in gas analysis for the absorption of oxygen.

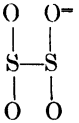
Hydrogen peroxide is reduced to water by hyposulfites. HNO_2, but not alkaline nitrites, react to form NO, NO_2, and H_2O; $HAsO_2$, in acid or alkaline solution, is reduced to metallic arsenic. The reaction with titanium compounds appears to be reversible:

$$2TiO^{++} + S_2O_4^{=} = 2Ti^{+++} + 2SO_3^{=}$$

The reaction between $S_2O_4^{=}$ and H_2S is said to take place rapidly according to the equation:

$$S_2O_4^{=} + H_2S = S_2O_3^{=} + S + H_2O$$

With regard to the structure of the hyposulfite ion, there is little doubt but that the two sulfur atoms are bonded together and that each sulfur atom is bonded to two oxygen atoms.



$$\begin{array}{ccc} O & & O^{-} \\ | & & | \\ S & - & S \\ | & & | \\ O & & O \end{array}$$

But further structural details await crystal-structure determinations.

The name "dithionous acid" has been suggested to replace the more common term "hyposulfurous acid" in order to conform to the customary rule of applying the name "hypo . . . ous" to that acid in which each atom of the acid-forming element is less oxidized by two valency stages than the corresponding atoms in the acid to which the name ending in "-ous" is given (compare *chlorous* with *hypochlorous acid; nitrous* with *hyponitrous acid*). The prefix "hypo" (from the Greek prefix for *under*) does not, however, always indicate an oxidation number lower by two. For example, phosphorus in hypophosphoric acid, $H_4P_2O_6$, has a valency one less than in phosphoric acid, H_4PO_4 [see the report of the Committee for Inorganic Chemical Nomenclature, *J. Am. Chem. Soc.*, **63,** 889 (1941)].

Dithionic acid, $H_2S_2O_6$

Since aqueous solutions of free dithionic acid tend to decompose slowly if heated, it is customary to carry out the preparations of the salts rather than that of the acid itself. An electrolytic method has been investigated by Essin [*Z. Electrochem.*, **34,** 78 (1928)] in which a solution containing Na_2SO_3 and not more than 0.1% NH_4F is electrolyzed between previously ignited platinum electrodes. The current yield does not exceed 50% and is more often around 40%, the remainder of the current being consumed in the oxidation of sulfite to sulfate.

The usual chemical method of preparation consists in passing sulfur dioxide into an aqueous suspension of manganese dioxide; the addition of SO_2 is continued until nearly all of the manganese dioxide is dissolved. Best results are obtained if the mixture is agitated frequently or continuously and if it is initially cool; the yield drops off if the mixture is warmed. Both sulfate and dithionate are formed in the reaction, which is approximately expressed by the equation:

$$2MnO_2 + 3SO_2 = MnSO_4 + MnS_2O_6$$

In reality, two main reactions appear to take place simultaneously, one producing dithionate and the other sulfate. A low temperature, around 0°, favors the formation of dithionate, and yields of over 90% are obtainable [compare J. Meyer and Schramm, *Z. anorg. Chem.*, **132,** 226 (1924)]. The ions present in the filtered reaction mixture are Mn^{++}, $S_2O_6^=$, $SO_4^=$, and some H_2SO_3, and the first of these can be removed by the addition of alkali. If $Ba(OH)_2$ is the alkali used, the manganese, sulfate, and sulfite are precipitated, and the filtered solution contains then only Ba^{++}, $S_2O_6^=$, and OH^-. Excess barium hydroxide is removed by treating with just enough sulfuric acid and filtering. The resulting solution may be crystallized to obtain the colorless, soluble salt, $BaS_2O_6 \cdot 2H_2O$. The barium salt may be converted to the salts of other metals by well-known methods. Aqueous solutions of the acid result when the barium salt in solution is treated with an equivalent amount of sulfuric acid. The preparation of the sodium salt can be made somewhat more direct in that one needs only to shake a mixture of aqueous $NaHSO_3$ and finely powdered MnO_2 until reaction is complete and then evaporate the filtered solution until the colorless $Na_2S_2O_6 \cdot 2H_2O$ crystallizes out [Sihvonen, *Z. phys. Chem.*, **20,** 276 (1923)].

A number of other oxidizing agents will convert sulfurous acid solutions partially to dithionate, among the important agents being $KMnO_4$, $Fe(OH)_3$, Fe^{+++}, $Co(OH)_3$, $Ni(OH)_3$, $Ce(SO_4)_2$, $Ru(SO_4)_2$, and H_2O_2, but this does not close the list. Indeed, an oxidizing agent that will not produce at least traces of dithionate is rare, and it is for this reason that a number of apparently attractive oxidimetric methods for the analysis of sulfites fail to yield quantitative results.

The solutions of dithionic acid are strongly acidic, there being no indication that the acid is in any way weak. The equivalent conductance at infinite dilution is $\Lambda_\infty = 437.3$ ohm^{-1} at 25°, while that for a 0.025 n solution is 392 ohm^{-1} and for a 0.5 n solution is 360 ohm^{-1} [Ostwald, *Z. phys. Chem.*, **1,** 106 (1887); Hertlein, *Z. phys. Chem.*, **19,** 287 (1896); for the conductivity of $Na_2S_2O_6$ solutions, see Watkins and Jones, *J. Am. Chem. Soc.*, **37,** 2629 (1915)]. Moreover, no acid salts of the dithionates are known. Until further evidence to the contrary appears, it must be assumed that both hydrogens in dithionic acid ionize freely and to about the same extent, and that, therefore, the acid is strong and dibasic. Measurements of the freezing-point lowering in solutions of barium and sodium dithionate [J. Meyer, *Ber.*, **34,** 3606 (1901)] throw little light on the ionization of dithionic acid; indeed, one can only conclude that the acid is dimeric and not monomeric, (HSO_3), a point that remained in doubt at one time. (*Cf.* the few but significant experiments of Hägg [*Z. phys. Chem.*, **18B,** 199 (1932)], who could find no inflections in the electrometric titration curves for dithionates, and in addition confirmed the dibasic character of the acid by freezing-point experiments with dilute solutions of $K_2S_2O_6$.)

Dilute solutions of dithionic acid do not decompose at room temperatures at an appreciable rate; but when attempts are made to concentrate the acid, decomposition according to the reaction

$$H_2S_2O_6 = H_2SO_4 + SO_2$$

prevents the preparation of solutions having a specific gravity much greater than 1.347. Stamm and Adolf [*Ber.*, **67,** 726 (1934)] evaporated solutions at 25° and 15 mm pressure and obtained a $1H_2S_2O_6 + 15H_2O$ mixture.

If dilute solutions of acidified dithionates are warmed to about 50° or higher, the rate of decomposition becomes measurable. The experimentally determined rate equation is [Yost and Pomeroy, *J. Am. Chem. Soc.*, **49,** 703 (1927)]:

$$-\frac{d(S_2O_6^=)}{dt} = k(H^+)(S_2O_6^=), \qquad k = 0.16 \text{ at } 80° \qquad k \approx 0.003 \text{ at } 50°$$

the time being expressed in minutes and concentrations in moles per liter of solution. At high acid concentrations ($H_2S_2O_6$ + HCl or $HClO_4$), $(\Sigma H^+) > 0.6$ n, the rate of decomposition becomes considerably greater than that predicted by this equation. The mechanism of the decomposition at all acidities is not at all certain, but for low acid concentrations one may consider as reasonable that the ion $HS_2O_6^-$ is the reactive species; and since its (low) concentration is determined by the (H^+), the rate equation found by experiment would be a consequence.

$$H^+ + S_2O_6^= = HS_2O_6^- \qquad \text{(rapid and reversible)}$$
$$HS_2O_6^- + H_2O = H_2SO_3 + HSO_4^-$$
$$\text{(rate-determining step)}$$

This kind of mechanism is favored by Stamm and Adolf [*Ber.*, **67,** 726 (1934)] and by J. Meyer [*Z. anorg. Chem.*, **222,** 337 (1935)], but, while considered, was not completely accepted by Yost and Pomeroy because the validity of the mass law, in the solutions of strong electrolytes present at rather high concentrations, seemed doubtful.

Dithionic acid reacts but slowly, if at all, with most oxidizing agents. It has been shown that at 50° the rate-determining step in the oxidation by dichromate, bromate, and iodate is the decomposition discussed above, the H_2SO_3 formed then reacting rapidly with the oxidizing agent [Yost and Pomeroy]. At room temperatures, $KMnO_4$, HClO, Cl_2, Br_2, I_2, and many other strong or moderately strong oxidizing agents have no effect on dilute dithionate solutions. Any apparent oxidation takes place as a consequence of the decomposition reaction. Both dithionic acid and its salts also resist reduction, as is evidenced by the fact that arsenites and stannous tin do not react with them. Zinc or sodium amalgam brings about reduction to sulfite and, eventually, to hyposulfite.

The salts of dithionic acid are quite stable and do not decompose on heating until a temperature of about 200° is reached. The decomposition then takes place quantitatively according to the equation [Litterscheid and Lowenheim, *Chem. Ztng.*, **48,** 881 (1924)]:

$$Na_2S_2O_6 = Na_2SO_4 + SO_2$$

Aqueous solutions of the salts do not decompose even on continued boiling; but on heating for several hours at 150–180° in a closed tube, complete decomposition takes place, with the formation of sulfate, sulfur dioxide, and sulfur.

All of the known salts of dithionic acid are soluble in water. The following table shows the solubilities of some of the more important salts at 20° in g of anhydrous salt per 100 g of solution [de Baat, *Rec. trav. chim.*, **45,** 237 (1926)].

TABLE 102
SOLUBILITIES OF SOME DITHIONATES IN WATER AT 20°

	Sol.		Sol.
$Na_2S_2O_6 \cdot 2H_2O$........	15.12 (100 g H_2O)	CaS_2O_6 $4H_2O$........	20 25
$K_2S_2O_6$..	6.23	MgS_2O_6 $6H_2O$........	33.91
$BaS_2O_6 \cdot 2H_2O$..	15.70	$Ag_2S_2O_6 \cdot 2H_2O$.......	≈ 50

CHAPTER 11

Hydrogen Peroxide, Hydrogen Persulfides, and the Peroxyacids. Metallic Peroxides and Superoxides. Polythionic Acids

Preparation of hydrogen peroxide

Solutions of hydrogen peroxide may be conveniently prepared in any one of the following ways. (1) Barium oxide is heated at 500–600°C in an atmosphere of oxygen, whereupon the reversible reaction

$$2BaO + O_2 = 2BaO_2$$

takes place [Hildebrand, *J. Am. Chem. Soc.*, **34,** 246 (1912)]. The barium peroxide is then decomposed with an acid, and this results in the formation of a solution of hydrogen peroxide and a barium salt. If sulfuric or carbonic acid is used, the barium sulfate or carbonate precipitates, and the peroxide alone remains in solution. When carbonic acid is used, the procedure consists in stirring powdered BaO_2 with water and passing a rapid stream of carbon dioxide into the stirred mixture. To ensure that the hydrogen peroxide solutions are free from impurities, the first solution should be distilled off; the distillate contains the hydrogen peroxide. Solutions of hydrogen peroxide may be concentrated to some 30% H_2O_2 by fractional distillation at atmospheric pressure. (2) Sodium peroxide, prepared by passing oxygen over heated metallic sodium or by heating sodium monoxide, Na_2O, in dry air, is slowly added in equivalent amount to cooled (0°), 20% sulfuric acid, and, after decanting from the precipitated $Na_2SO_4 \cdot 10H_2O$, the solution is distilled under reduced pressure. (3) A strong solution of ammonium or potassium bisulfate, $KHSO_4$, containing hydrofluoric acid (20%) or small amounts of $K_4Fe(CN)_6$, is electrolyzed. The resulting product consists of solid and dissolved potassium peroxydisulfate, $K_2S_2O_8$, but this may be decomposed to peroxymonosulfuric acid, H_2SO_5, and eventually hydrogen peroxide by the addition of sulfuric acid. The resulting solution is distilled as before.

Pure, anhydrous hydrogen peroxide is somewhat more difficult to prepare than the dilute or concentrated solutions. As noted above, fractional distillation at atmospheric pressure yields a product containing at most 30% H_2O_2, since continued distillation is accompanied by extensive decomposition and loss of peroxide. By carrying out the fractionation on the 30% product at low pressures, about 10 mm Hg, and low temperatures, 60°, solutions containing 90% or more of peroxide can be obtained. It is essential in this operation that impurities be absent and that the glassware used be carefully cleaned before undertaking the distillation. It is said to be helpful to "acidify" the glass by passing a stream of dry HCl followed by dry air through the apparatus, but experience has shown that this is not necessary with Pyrex glass. The ordinary impurities, HCl, K_2SO_4, and HNO_3, are removed by making the 30% peroxide slightly alkaline and then distilling; the distillate will, by this procedure, be freed from any non-volatile salts. This distillate is fractionated at low pressure and temperature, 60°, and the less volatile hydrogen peroxide is recovered at concentrations of 90% or greater.

The 90% solution can, to be sure, be further concentrated by distillation, but a point is reached (about 98%) where the rate of decomposition is large, so that further concentration becomes impracticable or impossible. Further purification is attained by fractional crystallization. The 90% (or more concentrated) solution is cooled to the freezing point (about −15°), when crystals of hydrogen peroxide separate out. By separating the crystals, melting, and partially freezing again, a product is eventually obtained which is pure or very nearly pure hydrogen peroxide. The method of fractional crystallization for the purification of hydrogen peroxide was worked out by Maass and Hatcher [*J. Am. Chem. Soc.*, **42,** 2548 (1920)], and by properly and systematically combining mother liquors and solids they were able to attain good yields of the anhydrous material.

A modified peroxysulfate method has been used by Fehér [*Ber.*, **72B,** 1789 (1939)] to prepare small amounts of concentrated D_2O_2 (99.7%). Heavy water vapor, D_2O, is passed into a mixture of D_2SO_4 and $K_2S_2O_8$ maintained at 70–90°. A mixture of D_2O and D_2O_2 distills over and is fractionated. The distillate is passed back into the D_2SO_4 and $K_2S_2O_8$ mixture, where its D_2O_2 concentration is enriched. By this cyclic process the expensive heavy water is fully utilized.

Preparation of hydrogen persulfide

The method of preparation of hydrogen persulfide, H_2S_2, is similar to the chemical methods for the preparation of hydrogen peroxide, in that a polysulfide is decomposed with a strong acid. In both cases the principle of the methods depends on the fact that the substances are weak acids; consequently, when a stronger acid is added to the salt, the undissociated persulfide or peroxide is formed.

$$Na_2S_2 = 2Na^+ + S_2^=$$
$$S_2^= + 2H^+ = H_2S_2$$

In fact, the acids H_2S_2 and H_2O_2 are so weak that their salts hydrolyze extensively, and aqueous solutions of them are quite alkaline.

The preparation of hydrogen persulfide has been investigated by Butler and O. Maass [*J. Am. Chem. Soc.*, **52**, 2184 (1930)], and they find that the yields depend on the composition of the sodium polysulfide used; a mixture of the composition corresponding to $Na_2S_{2.5}$ gives the highest yields. Their method of preparation is as follows: a mixture of 150 g of flowers of sulfur, 725 g of solid Na_2S, and 500 cc of distilled water is heated on a water bath until solution is complete, when 1300 cc of additional distilled water are added. One liter of the final solution is added slowly from a dropping funnel to 1500 cc of 1.19 c.p. hydrochloric acid; the acid is maintained at −15° and is stirred continually during the addition of the sulfide. The hydrogen persulfide forms an emulsion with the acid mixture, but this separates into two liquid layers after three hours' standing, the hydrogen persulfide being in the lower, oil-like, yellow layer. The yellow oil is washed with distilled water, solid phosphorus pentoxide is added, and after filtering, the oil is fractionally distilled at 120° under a pressure of 10 mm; the yellow oil consists of H_2S_2 and H_2S_3, and these two substances are separated in the distillation. Even at this temperature of distillation there is appreciable decomposi-

TABLE 103

THE PHYSICAL PROPERTIES OF H_2S, H_2S_2, H_2O, AND H_2O_2

Substance	Melting Point (°C)	Boiling Point (°C)	Heat of Evaporation (cal)[a] (Trouton's Constant)	Heat of Fusion (cal)	Density of Liquid
H_2S	−85.49	−60.33	4,463 (b.p.) (21.0)	568.1	0.964(−60°)
H_2S_2	−89.6	70.7 ± 5	8,544 (24.9)	1800	1.3339 (20°)
H_2O	0.00	100.0	9,730 (b.p.) (26.1)	1437	.9982 (20°)
H_2O_2	−0.89	151.4	11,610 (27.4)	2500	1.4418 (20°)

Substance	Viscosity	Surface Tension (dynes/cm)	Heat Capacity of Liquid (cal/mole/deg)	Dielectric Constant	ΔF°_{298} of Formation (cal)
H_2S		28.2 (b.p.)	16.32 (b.p.)	8.37 (−78.7°)	−7,865
H_2S_2		38.1 (b.p.)	22.1 (b.p.)	—	—
H_2O	0.01054 (18°)	75.5 (0°)	18.0 (18°)	84.4 (0°)	−56,693
H_2O_2	.01310 (18°)	78.7 (0°)	19.7 (18°)	93.7 (0°)	−28,230

[a] All thermochemical and thermodynamic constants refer to one formula weight of the substance in question.

tion of the persulfides into H_2S and sulfur. The yield is 36% H_2S_3 and 11% H_2S_2 when calculated from the amount of yellow oil distilled. The trisulfide may be decomposed ("cracked") slowly in the temperature range 75° to 125°, and by this procedure about one-half of the original trisulfide is recovered in the form of the disulfide.

The disulfide is further purified by distilling from P_2O_5 under vacuo in "acidified" quartz vessels. Glass apparatus may be used if "acidified," but the least decomposition results if quartz is employed.

Other persulfides of hydrogen

The hydrogen trisulfide H_2S_3, which is obtained as a by-product in the preparation of H_2S_2, is a mobile, yellow, oily liquid with an odor similar to that of camphor and sulfur monochloride. It solidifies to a glass at about −50°; attempts to distill it without decomposition, even at low pressures, have been unsuccessful [Walton and Parsons, *J. Am. Chem. Soc.*, **43**, 2539 (1921)]. The action of anhydrous formic acid on crystals of pure ammonium pentasulfide yields a thin, clear, yellow oil which has the composition H_2S_5. The molecular weight found in benzene solution was 152.5 (formula weight, 162); the oil could not be distilled without decomposition [Mills and Robinson, *J. Chem. Soc.*, 2326, (1928)]. All the persulfides dissolve sulfur readily. From a break in the solubility curve in both H_2S_2 and H_2S_3, Walton and Whitford concluded that the compound H_2S_6 exists below −1.45° [*J. Am. Chem. Soc.*, **45**, 601 (1923)]. The persulfides all dissolve readily in organic solvents such as benzene, chloroform, and ether, although impurities catalyze the decomposition. Their instability has so far prevented any accurate measurements of physical properties.

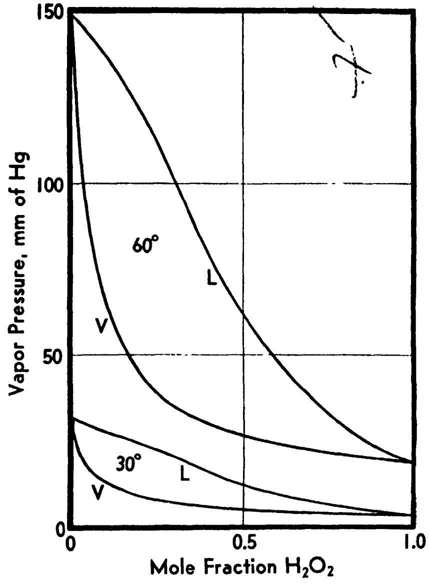


Fig. 70. The Vapor Pressure-Composition Diagram for the System $H_2O—H_2O_2$ at 30° and 60°C.

Physical properties of H_2O_2 and H_2S_2

The physical properties of hydrogen persulfide and peroxide are best exhibited together and along with those of hydrogen sulfide and water.

Tables 103 and 104 and Figures 70 and 71 contain the known data [H_2S_2, Butler and Maass, *J. Am. Chem. Soc.*, **52,** 2184 (1930); H_2O_2, references in the table; H_2S and H_2O, see Chapter 8].

The O—O distance in hydrogen peroxide has been found by electron diffraction to be 1.47 Å [P. A. Giguere and V. Schomaker, unpublished

TABLE 104
THE PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE

Anhydrous H_2O_2

Freezing point,[1] −0.89° Boiling point,[8] 151° (extrap.)

Density of Liquid,[2] ρ

t(°C)	−10	0	10	20
ρ (g/cc)	1.475	1.4649	1.452	1.442

Density of solid,[2] 1.643 g/cc (−4 to −8°)

Vapor Pressure of Liquid[3]

t(°C)	10	20	25	40	50	60	70	80	90
p_{mm}	0.8	1.5	2.1	5.7	10.4	18.1	29.7	47.4	71.5

$$\log_{10} p_{\text{mm}} = -\frac{2534.7}{T} + 8.853$$

Viscosity,[2] η

t(°C)	0.04	11.90	12.20	19.60
η (centipoise)	1.828	1.456	1.447	1.272

Surface Tension,[2] γ

t(°C)	0.2	6.2	11.0	13.9	18 2
γ (dynes/cm)	78.73	77.79	77.51	76.47	75.94

Specific heat,[2] liquid, 0.579 cal/g (0–18°); solid, 0.470 cal/g
Heat of vaporization,[2] 326 cal/g. Heat of fusion,[4] 79 cal/g
Heat of decomposition,[5] $H_2O_2(l) = H_2O(l) + \frac{1}{2}O_2$ (g, 1 atm), $\Delta H = -23{,}450$ cal at 20°
Dipole moment,[4] 2.1×10^{-18} e.s.u.
Dielectric constant,[5] 93.7 at 0°C
Refractive index,[2] 1.4139 at 22°C
Magnetic susceptibility,[6] -0.88×10^{-6} cgs units
Moments of inertia,[7] 2.78×10^{-40} g cm^2, smallest; 33.9×10^{-40} g cm^2, harmonic mean of other two.

TABLE 104 (*Cont.*)
Aqueous Solutions of H_2O_2

% H_2O_2	00	10	20	30	40	50	60	70	80	90	100
Mole fraction H_2O_2	0.00	.055	.117	.185	.265	.346	.443	.553	.679	.826	1.00

Densities[2] at 18°

% H_2O_2	0.00	22.33	56.70	73.44	90.42	100.00
ρ, g/cc	0.9986	1.0815	1.2270	1.3071	1.3953	1.4442

Boiling Point[8]

Mole fraction H_2O_2	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Boiling point (extrap.) (°C)	100.0 0.9 145.9	102.2 1.00 150.5	105.6	109.7	114.5	120.1	126.1	132.8	139 2

[1] Cuthbertson, Matheson, and Maass, *J. Am. Chem. Soc.*, **50**, 1120 (1928)
[2] Maass and Hatcher, *ibid.*, **42**, 2548 (1920)
[3] Maass and Hiebert, *ibid.*, **46**, 2693 (1924)
[4] Linton and Maass, *Can. J. Res.*, **7**, 81 (1932)
[5] Matheson and Maass, *J. Am. Chem. Soc.*, **51**, 674 (1929)
[6] Maass and Hatcher, *ibid.*, **44**, 2472 (1922)
[7] Zumwalt and Giguere, *J. Chem. Phys.*, **9**, 458 (1941)
[8] Giguere and Maass, *Can. J. Res.*, **18B**, 181 (1940)

research]. Calculations and spectroscopic studies have shown that there is one hydrogen on each oxygen and that the molecule cannot be linear; both the O—O—H angle and the angle between the O—O—H planes are about 100° [Penney and Sutherland, *J. Chem. Phys.*, **2**, 492 (1934); Fehér, *Ber.*, **72B**, 1778 (1939); Zumwalt and Giguere, *J. Chem. Phys.*, **9**, 458 (1941)]. In H_2S_2 the S—S distance has been found to be 2.05 Å. This value is in good agreement with the value 2.08 Å expected for a S—S single bond and in poor agreement with the value 1.90 Å expected for a double bond. The hydrogens are thus most probably on different sulfur atoms; the angles would be about the same as for H_2O_2 [Stevenson and Beach, *J. Am. Chem. Soc.*, **60**, 2872 (1938)].

Both hydrogen peroxide and persulfide are characterized by a large thermodynamic tendency to decompose into water and hydrogen sulfide and free oxygen and sulfur, respectively. In both cases, and in the absence of other catalysts, the decomposition is more rapid in the presence of alkalis than in an acidic environment. This explains why, in the preparation, the vessels employed must be "acidified," Pure hydrogen peroxide will decompose with explosive violence if dropped into a vessel heated to 153° or greater; at lower temperatures the decomposition proceeds more or less quietly.

The fact that pure hydrogen peroxide has properties much like those of water suggests that it may act as an ionizing solvent. It turns out that some salts, NaF, KCl, and K_2SO_4, are more soluble in pure hydrogen peroxide than in water, and the equivalent conductances (in tin vessels) of KCl solutions are of the same order of magnitude in both solvents. At 0° potassium chloride does not react with pure hydrogen peroxide and

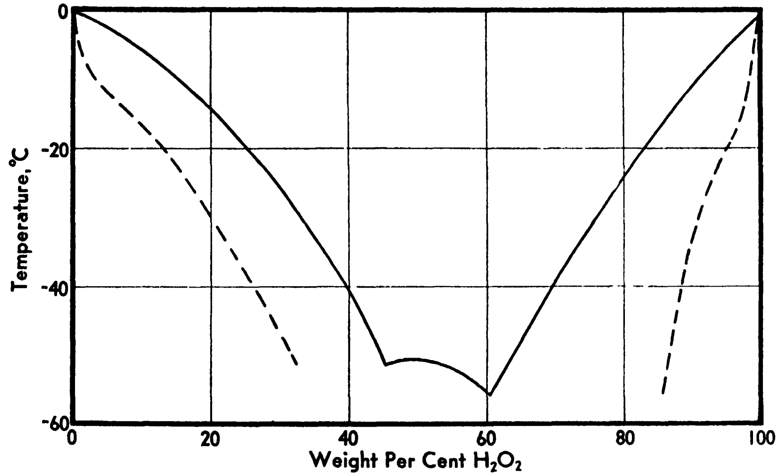


Fig. 71. The Phase Diagram for the System H_2O—H_2O_2. The dashed lines show the average composition of the solid phase (which is a solid solution) when approximately 20% of the melt has been crystallized.

$\Lambda_0 = 65.5$, the value in aqueous solution at the same temperature being 81.5. The degree of dissociation of KCl is nearly the same in both solvents at the same concentrations. The difference in Λ_0 for potassium chloride in the two solvents is in accord with the difference in their viscosities; in fact, $65.5 \times 0.0131 = 0.858$ and $81.5 \times 0.0105 = 0.855$ (see Table 104 for viscosities)—that is, Walden's Rule, $\Lambda_0'\eta_1 = \Lambda_0''\eta_2$, applies in this case, although it is deemed to be strictly valid only for ions of large diameters.

Hydrogen persulfide is doubtless characterized by a low dielectric constant, and hence it will probably be a good solvent only for non-polar compounds; any salts that dissolve in it will probably ionize but little. Characteristic of hydrogen persulfide is its ability to dissolve sulfur: 60.9 g of sulfur will dissolve in 100 g H_2S_2 at 22.7°, and the solution is not accompanied by the formation of any H_2S_3.

The chemical properties of H_2O_2

Hydrogen peroxide is a weak acid. The pure substance has for its ionization constant $(H^+)(HO_2^-) = K \approx 1.55 \times 10^{-12}$; that is, the concentration of hydrogen ion is about 12 times that in pure water and is about 0.06 of that in dilute solutions of boric acid. It is doubtless due to its acidic nature that such compounds as $NH_3 \cdot H_2O_2$ are formed when ammonia is added to pure hydrogen peroxide. With some of the organic amines, oil-like compounds are formed having the formula $RNH_2 \cdot 2H_2O_2$ [Matheson and Maass, *J. Am. Chem. Soc.*, **51,** 674 (1929)].

The reactions involving hydrogen peroxide in aqueous solutions are very large in number and of considerable interest; they may be classified as follows: (1) reactions in which H_2O_2 is formed, (2) reactions of H_2O_2 to form complex substances (peroxyacids), (3) oxidation reduction reactions.

1. Hydrogen peroxide appears to be formed by the reduction of elementary oxygen and not by the oxidation of oxide oxygen (exceptions: $BaO + \frac{1}{2}O_2$, $Na_2O + \frac{1}{2}O_2$, and electrolysis of $KHSO_4$ solutions). That is to say, we may expect to find peroxide formed only in reactions of the type:

$$\text{Reducing agent} + O_2 = \text{peroxide}$$

Thus, when the alkali metals react with oxygen, when metals such as zinc are shaken with water containing dissolved oxygen, and when some reducing agents in aqueous solutions, for example, $TiCl_3$, are exposed to the action of air or oxygen, peroxide is formed. The reaction with titanous chloride solutions is very striking. The solutions are initially purple, the natural color of titanous ion; and when shaken vigorously in an atmosphere of oxygen, the intensity of the color diminishes, because TiO^{++}, a colorless ion, is formed in the oxidation reaction. When the purple color just vanishes, the solution suddenly becomes orange-yellow in color as the result of the formation of peroxytitanic acid, H_2TiO_4. The yellow color does not appear until after all of the titanous ion has disappeared, because hydrogen peroxide is rapidly reduced by that substance. The reactions are:

$$2Ti^{+++}\ (\text{purple}) + O_2 + 2H_2O = 2TiO^{++}\ (\text{colorless}) + H_2O_2 + 2H^+ \quad (\text{slow})$$

$$2Ti^{+++} + H_2O_2 = 2TiO^{++} + 2H^+ \quad (\text{rapid})$$

$$TiO^{++} + H_2O_2 + H_2O = H_2TiO_4\ (\text{yellow-orange}) + 2H^+ \quad (\text{rapid, reversible})$$

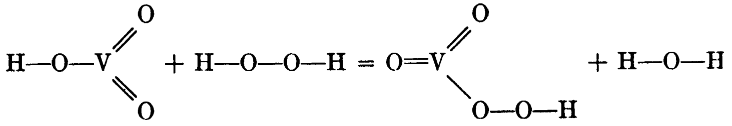
Reactions of this sort are very suggestive in that they raise the following question: Do all reactions involving the reduction of elementary oxygen give rise in the first step to the formation of peroxides? The answer is that peroxide is formed in some cases but not in others. Thus, the absorption of oxygen by the hemoglobin of the blood does not seem to be accompanied by the formation of any detectable peroxide. On the other hand, when benzaldehyde is exposed to the action of oxygen, a peroxide is known to be formed. The formation of peroxide in oxygen reduction reactions must, therefore, always be considered as a possibility, but it is not to be regarded invariably as an intermediate. The possibility that peroxide is a transitory intermediate and present, during the reduction of oxygen, at very small concentrations, must, naturally, be subjected to experimental test when feasible. Oxygen reactions are of great interest and importance in all fields of chemistry and deserve any attention given them.

2. When hydrogen peroxide is added to a solution of titanyl ion, TiO^{++}, the solution becomes yellow or yellowish-orange in color. The composition of the colored substance is not definitely known, but it is probably H_2TiO_4, peroxytitanic acid. Similarly, when hydrogen peroxide is added to acidified dichromate solutions, beautiful blue solutions result, and the blue substance may be extracted with ether, the ether solution also having a blue color of considerable beauty. The peroxychromic oxide formed has the formula CrO_5 [Schwartz and Giese, *Ber.*, **65B**, 871 (1932)]. Still another peroxyacid results when hydrogen peroxide is added to an acid solution of vanadic acid. Peroxyvanadic acid solutions have a pleasing red color, and the red compound has the formula HVO_4 [see T. Slater Price, *Peracids, and Their Salts;* W. Machu, *Das Wasserstoffperoxyd und die Perverbingdungen*].

The elements which form the complex peroxyacids are B, C, Ti, Zr, Sn, N, P, V, Cb, Ta, S, Cr, Mo, W, and U, that is, elements which are found only in the third to sixth groups of the periodic system. Simple peroxides are formed by several of the elements of the first and second groups.

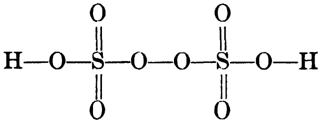
In a number of cases, the structures of the peroxyacids are rather simple and may be regarded as oxyacids in which one or more oxide oxygens have been replaced by a peroxide group $O{-}O^{=}$ or $-O{-}O-$; that is, they are simply coordination compounds, and the central atoms are not to be regarded as in higher valence states than correspond to their position in the periodic system. Thus, for peroxyvanadic acid, the reaction can be written:

$$HVO_3 + H_2O_2 = HVO_4 + H_2O$$



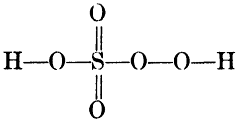
$$H{-}O{-}V\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{smallmatrix} + H{-}O{-}O{-}H = O{=}V\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown O{-}O{-}H\end{smallmatrix} + H{-}O{-}H$$

The formal structures of the peroxysulfuric acids would be:



$$\mathrm{H{-}O{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}{-}O{-}O{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}{-}O{-}H}$$

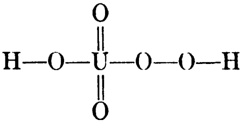
Peroxydisulfuric acid



$$\mathrm{H{-}O{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}{-}O{-}O{-}H}$$

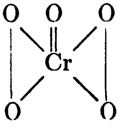
Peroxymonosulfuric acid

and that of peroxyuranic acid, H_2UO_5:

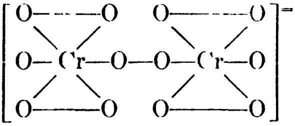


$$\mathrm{H{-}O{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{U}}{-}O{-}O{-}H}$$

The peroxychromic acids and salts do not appear to have such simple structures as those given above. One might expect them to have such formulas as H_2CrO_5 and $H_2Cr_2O_8$, corresponding to the peroxysulfates, but the molecular weights obtained for the substances $C_5H_5NCrO_5$ and $(NH_4)_3CrO_8$ indicate that the simplest compounds have the formulas CrO_5 and possibly H_3CrO_8 [Riesenfeld, *Ber.*, **41**, 3941 (1908)]. Thus, the molecular weight of $C_5H_5NCrO_5$ in the non-ionizing solvent benzene is found to be 211 ± 5, the formula weight being 211. Recent investigations by Schwartz and Giese [*Ber.*, **65B**, 871 (1932)] have established that the formula of the blue peroxychromate formed in acid solution may be represented simply by CrO_5 and that the formula $HCrO_6$ appearing in the older literature is incorrect. The compound formed when CrO_5 in ether solution is reacted with pyridine is $C_5H_5N{\cdot}CrO_5$ and not $C_5H_5NH{\cdot}CrO_5$, as was formerly supposed. The blue ether solutions appear to contain the complex $(C_2H_5)_2O{\cdot}CrO_5$. Magnetic susceptibility measurements on $C_5H_5N{\cdot}CrO_5$ show it to be paramagnetic with values of χ_m ranging from 160×10^{-6} to 330×10^{-6} cgs units at 20°, these variable values being less than correspond to even a single unpaired electron spin (1300×10^{-6}) [Klemm and Werth, *Z. anorg. Chem.*, **216**, 127 (1933)]. It is believed that the small paramagnetism is due to chromium impurities (trivalent chromium) and that pure $C_5H_5N{\cdot}CrO_5$ would be diamagnetic; in this event, hexavalent chromium is indicated, and the structural formula for CrO_5 would be:

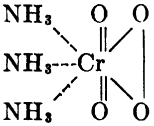


When ice-cold solutions of ammonium dichromate are treated with 30% hydrogen peroxide and potassium or thallium salts, the compound $Tl_2Cr_2O_{12}$ or $K_2Cr_2O_{12}$ separate out. The latter is diamagnetic [Klemm and Werth, *loc. cit.*], which suggests that the chromium is hexavalent in this compound also. The structural formula of the negative ion is probably:

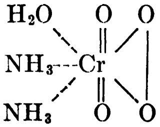


In acid solution, the addition of peroxide to dichromates leads to the formation of the blue peroxychromic acids which have just been discussed. When 30% hydrogen peroxide is added to a cooled, alkaline chromate solution (50 cc of 25% ammonia solution, 25 cc of 50% chromic acid solution, and 75 cc of water are mixed, and to the mixture is added dropwise 25 cc 30% H_2O_2), a reddish-yellow solution that eventually becomes brownish-black is formed. On standing one or two hours, reddish-brown crystals separate which, after washing with alcohol and then ether, are found to be well crystallized and to have the composition corresponding to $(NH_4)_3CrO_8$. The sodium and potassium salts have also been prepared. These salts and their alkaline solutions are known as the red peroxychromates [see Riesenfeld, Wohlers, and Kutsch, *Ber.*, **38,** 1885 (1905); Riesenfeld, *Z. anorg. Chem.*, **74,** 48 (1912); Spitalsky, *Ber.*, **43,** 3187 (1910)]. According to the measurements of Tjabbes [*Z. anorg. Chem.*, **210,** 385 (1933)], the red peroxychromates are paramagnetic, the value of χ_m being 1182×10^{-6} cgs units at room temperature. This fact indicates that pentavalent chromium is present in these compounds.

Another fundamental type of peroxychromic acid is formed when the mixture, solution and crystals, obtained in the preparation of $(NH_4)_3CrO_8$ is heated to 50° and then cooled to 0°. Long, brown crystals of $CrO_4 \cdot 3NH_3$ separate out, and it has been established that the ratio of hydrogen to nitrogen is 3:1. This compound presents no structural difficulty. From chromium trioxide, CrO_3, one may formally derive CrO_4 by replacing an oxide oxygen with a peroxide group. The three ammonias are thought to be bound as in ordinary coordination compounds [Riesenfeld, *Ber.*, **41,** 3536 (1909)]:



By reacting hydrogen peroxide in ethylacetate at 0° with an excess of CrO_3, a blue solution is obtained from which, on addition of ammonia, unstable tan crystals of the composition $H_2CrO_5 \cdot 2NH_3$ are precipitated [Nicholson, *J. Am. Chem. Soc.*, **58,** 2525 (1936)]. This may be still another type of peroxychromic compound, but it is likely that it is similar to the chromium tetroxide triammine of the preceding paragraph.



The peroxychromic acids in and out of solution are unstable and decompose slowly with the evolution of oxygen. This fact presents a stumblingblock in the way of closer investigation of these substances. The solid salts and coordination compounds are frequently explosive or inflame spontaneously in air.

Peroxymonosulfuric acid is formed when 30% hydrogen peroxide is added to concentrated sulfuric acid at room temperature. The reaction is reversible but somewhat slow. Preliminary measurements of the equilibrium constant have been made, but no accurate value can be given because of the uncertainties in the values of the activity coefficients of the reactants. The value $K = (H_2SO_4)(H_2O_2)/(H_2SO_5)(H_2O) \approx \frac{1}{3}$ was obtained by Ahrle [*J. prakt. Chem.*, **79,** 129 (1909)]. The reaction is

$$H_2O_2 + H_2SO_4 = H_2SO_5 + H_2O$$

Dilute solutions of H_2SO_5 decompose slowly at room temperatures and more rapidly at higher temperatures into hydrogen peroxide and sulfuric acid. The peroxymonosulfuric acid is distinguished, in sulfuric acid solution, from hydrogen peroxide by the reaction with permanganate; hydrogen peroxide is readily oxidized, while the peroxymonosulfuric is not affected. H_2SO_5 also reacts much more rapidly with iodide than does hydrogen peroxide [see, *e.g.*, Price, *J. Chem. Soc.*, **89,** 54 (1906); Willstatter and Hauenstein, *Ber.*, **42,** 1839 (1909)].

Anhydrous peroxydisulfuric acid is formed when chlorsulfonic acid, HSO_3Cl, and anhydrous hydrogen peroxide are mixed [D'Ans and Friedrich, *Z. anorg. Chem.*, **73,** 345 (1912)].

$$2HSO_3Cl + H_2O_2 = H_2S_2O_8 + 2HCl$$

The anhydrous acid forms small white crystals which melt at 65° with decomposition. H_2SO_5 is also formed in the reaction and is a beautifully crystalline solid melting without decomposition at 45°. When kept dry, both of the anhydrous peroxysulfuric acids decompose only slowly; but when decomposition is once started, the rate increases.

Peroxydisulfuric acid solutions are commonly prepared by the electrolysis of bisulfates, the best yields being obtained with the ammonium and potassium salts. It is supposed that the HSO_4^- is discharged at the anode to form, momentarily, HSO_4, and this combines immediately with another discharged ion to form $H_2S_2O_8$. This mechanism may be a helpful aid to the memory, but it cannot be regarded as having been established. For reasons not well understood, the yield of peroxydisulfates is increased nearly twofold if hydrofluoric or hydrochloric acid or $K_4Fe(CN)_6$ is added to the electrolyte. The yield also increases with overvoltage, and the added substances promote high overvoltages. High current densities lead to high yields, at least in the electrolysis of ammonium bisulfate; 300 amp/cm² will result in a current yield of 70%, providing the electrolyte is kept acid. Bright platinum electrodes lead to higher yields than do platinized ones, the difference in overvoltage again being responsible for the difference in yield.

Potassium peroxydisulfate is only moderately soluble in water, 4.08 g/100 g H_2O at 40°, and consequently this salt precipitates out as it forms in the electrolytic process. The salt is crystalline and, at room temperatures, does not decompose. It is an article of commerce. Its aqueous solutions are neutral, and the acid itself is therefore strong. On heating to 70° or higher, aqueous solutions of the acid or the salt slowly decompose. The rate of decomposition in solution has been measured and found to be first-order with respect to peroxydisulfate ion, that is,

$$S_2O_8^{=} + H_2O = 2HSO_4^{-} + \tfrac{1}{2}O_2$$

$$-\frac{d(S_2O_8^{=})}{dt} = k(S_2O_8^{=})$$

Temp. (°C) . .	70	80	90
k (min⁻¹)	0 0016	0 0055	0 0161

The rate of decomposition increases with the acid concentration of the solutions [Green and Masson, *J. Chem. Soc.*, **97**, 2083 (1910)].

The ammonium salt is much more soluble than the potassium salt, the solubility of the former being 58.2 g/100 g H_2O at 0°. At room temperatures the ammonium salt does not decompose; it too is an article of commerce. On heating it or its solutions, there result both decomposition and the oxidation of the ammonium ion to nitrogen and oxides of nitrogen.

In strong sulfuric acid solutions, peroxydisulfuric acid or its salts hydrolyze to give the monoacid

$$S_2O_8^{=} + H_2O = SO_5^{=} + SO_4^{=} + 2H^+$$

The rate of hydrolysis increases with increase in temperature. On dilution of the concentrated sulfuric acid, the monoacid in turn hydrolyzes extensively to hydrogen peroxide and sulfuric acid, and the former may be distilled from the solution. The series of reactions, electrolysis of bisulfates, hydrolysis to the monoacid and then to hydrogen peroxide, followed by distillation, form the basis of a commercial method for the manufacture of hydrogen peroxide solutions.

Peroxydisulfates are very strong oxidizing agents, the normal electrode potential being about two volts. Notwithstanding this great oxidizing strength, many of the oxidation reactions are slow, a characteristic that is another good illustration of the fact that reactions may have a strong tendency to take place while their rates may be slow. All oxidation reactions of peroxydisulfates are not slow, however; for example, the reaction with ferrous iron

$$S_2O_8^{=} + 2Fe^{++} = 2SO_4^{=} + 2Fe^{+++}$$

is so rapid that measurements of its rate are difficult; the reaction is second-order [Saal, *Rec. trav. chim.*, **47**, 385 (1928)].

$$-\frac{d(S_2O_8^{=})}{dt} \approx 500\ (S_2O_8^{=})(Fe^{++}) \qquad (13°C;\ \text{conc. in moles/liter})$$

The reaction with cyanide ion is moderately rapid, and, if excess ammonia is present, just 75% of the cyanide is oxidized to carbamide; the reaction is useful in the quantitative estimation of cyanides.

Thiosulfate ion is oxidized slowly to tetrathionate if the peroxydisulfate is present in excess; if thiosulfate is in excess, trithionates are also formed. This statement is true only for concentrated solutions; if the solutions are dilute, only tetrathionate is formed. In dilute solutions, the rate of the reaction

$$S_2O_8^{=} + 2S_2O_3^{=} = 2SO_4^{=} + S_4O_6^{=}$$

is independent of the concentration of thiosulfate and first-order with respect to $S_2O_8^{=}$ [King and Steinbeck, *J. Am. Chem. Soc.*, **52**, 4779 (1930)].

$$-\frac{d(S_2O_8^{=})}{dt} = k(S_2O_8^{=})$$

The value of k depends on the purity of the water and the chemicals used in making up the solutions, a fact that suggests that the reaction is catalyzed. Several substances do act as catalysts for the reaction; for example, Cu^{++} has a strong effect, Fe^{+++} somewhat less, and I^- less still. The mechanism of the catalyzed reactions is as follows: the thiosulfate reduces the catalyst, cupric ion, for example, to Cu^+, and this ion, or the complex ion $Cu(S_2O_3)_2^{\equiv}$, is oxidized to cupric ion by the peroxydisulfate

$$S_2O_8^{=} + 2Cu^+ = 2SO_4^{=} + 2Cu^{++} \qquad \text{(slow)}$$
$$2Cu^{++} + 2S_2O_3^{=} = 2Cu^+ + S_4O_6^{=} \qquad \text{(rapid)}$$

The reaction catalyzed by iodine is of the same type,

$$\begin{aligned} S_2O_8^{=} + 2I^- &= 2SO_4^{=} + I_2 && \text{(slow)} \\ I_2 + 2S_2O_3^{=} &= 2I^- + S_4O_6^{=} && \text{(rapid)} \end{aligned}$$

From the results of measurements, it is possible to determine the rates of the rate-determining steps. Both are found to be second-order, that is,

$$-\frac{d(S_2O_8^{=})}{dt} = k(S_2O_8^{=})(Cu^+)$$

$$-\frac{d(S_2O_8^{=})}{dt} = k(S_2O_8^{=})(I^-)$$

The above chemical equations do not express the detailed mechanism of the slow steps. In the case of the iodide catalysis, the mechanism is probably expressed by

$$\begin{aligned} S_2O_8^{=} + I^- + H_2O &= 2SO_4^{=} + HIO + H^+ && \text{(slow)} \\ HIO^- + H^+ + I^- &= I_2 + H_2O && \text{(rapid)} \end{aligned}$$

or

$$\begin{aligned} S_2O_8^{=} + I^- &= S_2O_8I^{\equiv} && \text{(rapid, reversible)} \\ S_2O_8I^{\equiv} + I^- &= 2SO_4^{=} + I_2 && \text{(slow)} \end{aligned}$$

The liberated iodine then acts to oxidize thiosulfate ion rapidly to tetrathionate ion.

The reaction between $S_2O_8^{=}$ and S_2O_3 catalyzed by ferric salts is complicated by the fact that the ferric ion hydrolyzes if the solutions are neutral, and the thiosulfate decomposes if the solutions are acid.

Table 105 contains representative data for the uncatalyzed reaction and the catalyzed reaction between peroxydisulfate and thiosulfate for the case in which the added catalyst is iodide ion [King and Steinbeck, *J. Am. Chem. Soc.*, **52**, 4779 (1930)].

TABLE 105

KINETICS OF THE REACTION BETWEEN $S_2O_8^{=}$ AND $S_2O_3^{=}$ AT 25°

$$-\frac{d(S_2O_8^{=})}{dt} = k_0(S_2O_8^{=})$$

$K_2S_2O_8 = 0.01$ m
$Na_2S_2O_3 = 0.02$ m
(no added catalyst)

Redistilled Water Used in Making up Solutions

Conc. of added KCl	0.0 m	0.02 m	0.06 m
k_0^a	0.000191	0.000262	0.000427
k_0	.000182	.000270	.000443
k_0		.000283	.000480

TABLE 105 (*Cont.*)

Ordinary Distilled Water Used in Making up Solutions

Conc. of added KCl	0.0 m	0.02 m	0.06 m
k_0	0.000357	0.000444	0.00132
k_0	.000341	.000437	.00106
k_0	.000255	.000424	
k_0	.000595	.000171	
k_0	.000606	000733	

[a] The variation in k_0 in each column indicates the extent of reproducibility of the rate measurements.

$$-\frac{d(S_2O_8^{=})}{dt} = k_2(I^-)(S_2O_8^{=}) + k_0(S_2O_8^{=}) \quad \text{(catalyst, I}^-\text{, added)}$$

$$k_2(I^-) + k_0 = k_1$$

Redistilled Water Used in Making up Solutions

$K_2S_2O_8 = 0.01$ m $\quad Na_2S_2O_3 = 0.02$ m

$KCl + KI = 0.02$ m

Conc. KCl	Conc. KI	k_1	k_2
0.016 m	0.004 m	0 000954	0 173
.012	.008	.00159	.162
.008	012	00229	166
.004	.016	00294	.167
.0	.02	.00361	.167

$KCl + KI = 0.06$ m

Conc. KCl	Conc. KI	k_1	k_2
0.056 m	0.004 m	0.00125	0.203
.048	012	.00294	.208
04	02	.00477	216

The same reaction when catalyzed by copper sulfate is considerably more rapid than when catalyzed by iodide. Thus, at 25° and with concentrations of $CuSO_4$ (added) varying between 0.05×10^{-5} m and 2.5×10^{-5} m, the results shown in Table 106 were obtained. It is of interest that accurate values of the constant k_3 for a very rapid reaction are obtained here through measurements on a slow reaction.

The rates of both the catalyzed and uncatalyzed oxidations of thiosulfate depend on the ionic strength of the solutions. The dependence in the case of the iodide ion-catalyzed reaction is in qualitative agreement

TABLE 106

KINETICS OF THE REACTION BETWEEN $S_2O_8^=$ AND $S_2O_3^=$ CATALYZED BY $CuSO_4$ AT 25°

$$-\frac{d(S_2O_8^=)}{dt} = k_3(Cu^+)(S_2O_8^=) + k_0(S_2O_8^=)$$

$$k = k_0 + k_3(Cu^+)$$

$K_2S_2O_8 = 0.01$ m $\quad Na_2S_2O_3 = 0.02$ m

$Cu^+ = 0.05 \times 10^{-5}$ to 2.5×10^{-5} m

Redistilled Water Used in Making up Solutions

Conc. KCl	0.0	0.02	0.06
k_3	458	527	717

with the predictions of the Brönsted theory, since the rate constant k_2 increases with ionic strength. The fact that the uncatalyzed reaction has a "salt effect" is strong evidence for the belief that a small amount of negative ion is present as an impurity and is acting as a catalyst. This is shown by the increase in k_0 with ionic strength. It would appear that both distilled water and the solutions to which Cu^{++} was added contained a negatively charged ion which reacted with $S_2O_8^=$ in the first or primary step in the reaction. The nature of this negative ion is not known; but since thiosulfate ions form complexes readily with metal ions, it is to be supposed that a complex substance of the general formula $M_m^+(S_2O_3^=)_n$ and having a net negative charge is present in the solutions. The metal ion M^+ would be Cu^+, for the most part, when copper salts are added to the reaction mixture (*cf.* Table 106). In the case of simply distilled water, the nature of M^+ cannot be stated without further experimental evidence.

Iodide ion is slowly oxidized to iodine by $S_2O_8^=$, and the reaction has been carefully studied by King and Jacobs [*J. Am. Chem. Soc.*, **53,** 1704 (1931)] with special reference to the effect of the ionic strength, μ, of the reacting mixture. The rate is given by the differential equation

$$-\frac{d(S_2O_8^=)}{dt} = k(S_2O_8^=)(I^-)$$

and the mechanism is believed to be that given above, or

$$S_2O_8^= + I^- + H_2O = 2SO_4^= + HIO + H^+ \qquad \text{(slow)}$$
$$HIO + H^+ + I^- = I_2 + H_2O \qquad \text{(rapid)}$$

According to the Brönsted theory of reaction rates in solution, the value of k should increase with the ionic strength, and the results in Table 105 are in complete accord with this prediction. The older measurements of Price (see *Peracids and Their Salts*) and others at moderate concentrations led to

$$-\frac{d(S_2O_8^=)}{dt} = k(S_2O_8^=)(I^-)$$

with $k = 0.13$ to 0.19 at room temperature, the larger value corresponding to the highest concentrations, that is, to high ionic strengths; $\mu = \frac{1}{2}\Sigma C_i Z_i^2$, where C_i is the concentration and Z_i the charge of the i^{th} ion. In general, in presence of added univalent salts, $\log_{10} k = 1.075 + 2\sqrt{\mu}$, and $k_0 = 0.0841$, where k_0 now refers to the limiting case $\mu = 0$.

The results shown in Table 105 were published by King and were obtained with solutions containing thiosulfate so that no free iodine was ever present in detectable amounts; that is, $(I^-) =$ constant during a run. When $S_2O_8^=$ and I^- alone are mixed, iodine accumulates and is present as I_3^-. Two reactions appear then to be taking place simultaneously, namely, that between $S_2O_8^=$ and I^- and I_3^-, so that,

$$\begin{aligned}-\frac{d(S_2O_8^=)}{dt} &= k_1(S_2O_8^=)(I^-) + k_2(S_2O_8^=)(I_3^-)\\ &= k_1(I^-) + k_2(I_3^-)(S_2O_8^=)\end{aligned}$$

At 25° with $K_2S_2O_8 = 0.005$ m, and $KI = 0.01$ m, $k_1 = 0.125$ and $k_2 = 0.0645$; with added $KNO_3 = 0.10$ m, $k_1 = 0.265$ and $k_2 = 0.129$ [Jette and King, *J. Am. Chem. Soc.*, **51**, 1035 (1929)]. Time is expressed in minutes and concentrations in moles per liter of solution. Both k_1 and k_2 increase with ionic strength, and this is to be expected for the reactions postulated.

Of great interest is the effect of silver ion on the rates of a number of reactions involving peroxydisulfate. For example, at room temperature, peroxydisulfate does not oxidize manganous ion, chromic ion, vanadyl ion, oxalic acid, hydrazine, or ammonia; but if silver nitrate is added to the solutions, these substances are slowly oxidized to permanganate and manganese dioxide, dichromate, vanadate, carbon dioxide, nitrogen, and some nitric oxide or nitric acid, respectively. The mechanism of these reactions was first established by Yost and found to consist of two principal steps,

$$S_2O_8^= + Ag^+ = 2SO_4^= + Ag^{+++} \qquad \text{(slow)}$$

$$Ag^{+++} + \text{Reducing agent} = Ag^+ + \text{Oxidized form of reducing agent} \qquad \text{(rapid)}$$

If no reducing agent (other than silver ion) is present, a black precipitate of Ag_2O_3 is slowly formed; this precipitate slowly decomposes to black AgO and eventually to Ag_2O, or Ag^+ if the solution is acid. (In concentrated HNO_3, the Ag_2O_3 is soluble.) It is easily shown by experiment that Ag_2O_3 is capable of rapidly oxidizing any of the reducing agents mentioned. Accordingly, both from a study of reaction rates and from experiments on the nature of the Ag_2O_3, the mechanism of the silver-catalyzed reactions seems well established. The rate equation of the slow reaction is

$$-\frac{d(S_2O_8^=)}{dt} = k(Ag^+)(S_2O_8^=)$$

That is, the rate is independent of the concentration of reducing agent, Mn^{++}, Cr^{+++}, VO^{++}, and so forth, and this is in accord with experiment. The mechanism stated requires that k should be independent of the reducing agent present; the following Table 107 shows this to be true for several reducing agents [Dekker, Lévy, and Yost, *J. Am. Chem. Soc.*, **59**, 2129 (1937)], the values of k being, at equal ionic strengths, very nearly equal.

TABLE 107

REACTIONS OF $S_2O_8^=$ CATALYZED BY SILVER ION AT 25°

$$-\frac{d(S_2O_8^=)}{dt} = k(Ag^+)(S_2O_8^=)$$

Reducing Agent	Initial Ionic Strength	k^a
Cr^{+++}	0.234	0.341
	.485	.319
VO^{++}	.0595	.578
	.587	.334
	1.930	.204
Mn^{++}	0.0990	.491
	.570	.266
	1.899	.217
Hydrazine	0.200	.555
	.945	.340

[a] Time is expressed in minutes and concentrations in moles per liter of solution.

In some cases, the values of k are quite different from those given in Table 107. For example, oxalate ion is much more rapidly oxidized by $S_2O_8^= + Ag^+$ than would be expected if one judged solely from the results of the measurements cited in the table. Also, the oxidation of ammonia is several times more rapid than the hydrazine, chromic ion, or vanadyl ion oxidations. The explanation is to be found in the state of the catalyst, silver ion. In the ammonia solution, silver is present mainly as $Ag(NH_3)_2^+$, and this reacts with $S_2O_8^=$ at a different rate than does Ag^+.

$$S_2O_8^= + Ag(NH_3)_2^+ = 2SO_4^= + Ag^{+++} + 2NH_3 \qquad \text{(slow)}$$
$$S_2O_8^= + Ag^+ = 2SO_4^= + Ag^{+++} \qquad \text{(slower)}$$

$$-\frac{d(S_2O_8^{=})}{dt} = k_1(S_2O_8^{=})(Ag(NH_3)_2^+) + k_2(S_2O_8^{=})(Ag(NH_3)_3^+) = \{k_1(Ag(NH_3)_2^+) + k_2(Ag(NH_3)_3^+)\}(S_2O_8^{=})$$

But

$$Ag(NH_3)_2^+ + NH_3 = Ag(NH_3)_3^+ \qquad \text{(rapid, reversible)}$$
$$(Ag(NH_3)_3^+) = K(Ag(NH_3)_2^+)(NH_3)$$

Hence,

$$-\frac{d(S_2O_8^{=})}{dt} = \{k_1 + k_2K(NH_3)\}(Ag(NH_3)_2^+)(S_2O_8^{=})$$

and the rate constant for each run, $k = k_1 + k_2K(NH_3)$, is a linear function of the ammonia concentration. At 25°, $k_1 = 3.70$ and $k_2K = 23.0$ are representative values. When these are compared with the rate constants in Table 107, it is immediately seen that, with ammonia as the reducing agent, the rate is ten or more times as rapid as is the case when the reducing agent does not form a complex ion with silver.

The important principle exemplified by these results is that the nature of the reacting ion can have a large effect on the rate of the reaction in which it takes part. A common example of this is the action of oxygen on ferrous iron; in acid solution, the reaction is much slower than in alkaline solution. That is, the rate of $O_2 + Fe^{++}$ is slower than that of $O_2 + Fe(OH)_2$.

The properties of other peroxyacids are not so striking as those of H_2TiO_4, HVO_4, $HCrO_5$, H_3CrO_8, H_2SO_5, and $H_2S_2O_8$. Some, K_2CO_4 or $K_2C_2O_6$ and $NaBO_3$, are articles of commerce; in solution they decompose extensively into hydrogen peroxide and the oxyacid. Peroxynitric acid, HNO_4, appears to result from the action of pure H_2O_2 on N_2O_5 [D'Ans, *Z. Electrochem.*, **17**, 850 (1911)]; the compound is unstable and explosive. HNO_4 appears to be formed also when sodium nitrite solutions are mixed with acidified hydrogen peroxide. The peroxytantalates and columbates are fairly stable and may be prepared in solution by warming a mixture of acidified peroxide and the pentoxide Ta_2O_5 or Cb_2O_5. They are colorless.

As stated at the beginning of this section, the peroxyacids may be regarded as complex compounds derived from oxyacids by replacing an oxide oxygen by the peroxide group. Another way of looking at them is as follows: when an acid anhydride combines (reversibly) with water, an oxyacid results. For example,

$$H_2O + SO_3 = H_2SO_4$$

If, on the other hand, the anhydride reacts with hydrogen peroxide, a peroxyacid is formed, for example,

$$H_2O_2 + SO_3 = H_2SO_5, \qquad \text{and} \qquad H_2O_2 + 2SO_3 = H_2S_2O_8$$

In any event, the peroxyacids are not to be regarded as compounds containing the central atom in a higher oxidized state.

3. The reactions in which hydrogen peroxide acts as an oxidizing or reducing agent are large in number, and only a few representative examples can be mentioned here. In some cases hydrogen peroxide acts simply as a reducing agent; for example, at room temperature and in acid solution, permanganate is quantitatively reduced to manganous ion, and the reaction forms the basis for the quantitative estimation of hydrogen peroxide. Manganese dioxide is also reduced by H_2O_2 if the solution is acid; but $Mn(OH)_2$, on the other hand, is oxidized to MnO_2 if the solution is neutral or alkaline.

The most common reaction in which H_2O_2 acts as an oxidizing agent is that with iodide ion. Iodine is liberated. This reaction is often used as a test for peroxide, but unfortunately it is not a satisfactory one, in spite of its common use. TiO^{++} in acid solution will give an orange-yellow color with H_2O_2. This test is sensitive and much more reliable than the iodine test. Many substances liberate iodine from iodides; only a few, if any, give the orange-yellow color with TiO^{++}. The peroxide-iodide reaction is not always a simple reduction of peroxide; the peroxide can also act as a reducing agent under some conditions. In acid solution, the reaction

$$H_2O_2 + 3I^- + 2H^+ = I_3^- + 2H_2O$$

takes place; and if the concentration of H^+ is about 0.2 n or greater, the reduction of H_2O_2 is quantitative. (At higher (H^+), and in the presence of oxygen, the side reaction $4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$ gives rise to serious errors in iodimetric determinations.) The rate equation is

$$-\frac{d(H_2O_2)}{dt} = \{k_1 + k_2(H^+)\}(H_2O_2)(I^-) \begin{Bmatrix} k_1 = 0.60 \\ k_2 = 16 \end{Bmatrix} \text{ at } 25°$$

The rate-determining reactions are

$$\begin{aligned} H_2O_2 + I^- &= IO^- + H_2O \quad \text{at low } (H^+) \\ H^+ + H_2O_2 + I^- &= HIO + H_2O \quad \text{at high } (H^+) \end{aligned}$$

At low acid concentrations, two reactions contribute measurably to the oxidation of H_2O_2; namely,

$$\begin{aligned} H_2O_2 + HIO &= O_2 + I^- + H^+ + H_2O \qquad k_3 = 3.3 \times 10^5 \text{ at } 25° \\ H_2O_2 + IO^- &= O_2 + I^- + H_2O \qquad k_4 = 1 \times 10^{11} \text{ at } 25° \end{aligned}$$

When the rate of disappearance of H_2O_2 through these two reactions is the same as that through the two reactions of reduction above, we have, as a net result, the catalytic decomposition of hydrogen peroxide.

Ordinarily the hydrolytic reaction

$$I_2 + H_2O = H^+ + I^- + HIO$$

is considered very rapid, so that the only rate-determining reactions in the decomposition of H_2O_2 would be the two sets above. It turns out, however, that the situation is not so simple as this. In fact, Abel [*Z. physik. Chem.*, **136**, 161 (1928)] was forced to assume, in order satisfactorily to explain his results, that another rate-determining step is the hydrolytic reaction. Indeed, he concluded that for

$$I_2 + H_2O = HIO + H^+ + I^-, \qquad -\frac{d(I_2)}{dt} = k(I_2) \qquad k = 0.25 \text{ at } 25°$$

Since the equilibrium constant is $K = 3 \times 10^{-13}$, the rate constant for the reverse reaction will be 0.8×10^{12} [see Bray, *Chem. Rev.*, **10**, 161 (1932)]. Now if hydrogen peroxide and potassium iodide solutions are mixed, the conditions for the catalytic decomposition are realized; that is, the solution is nearly neutral, and both the oxidation and the reduction of peroxide occur simultaneously. From what has been said above, the general nature of the catalysis is understandable. In all of its details, the peroxide-acid-iodide kinetic system is not simple, however, and account must be taken of other factors if a complete explanation of the experimental facts is desired. For further details, the reader is referred to the papers of Abel and Bray.

Another reaction in which peroxide is reduced is that with iodine alone. If dilute acid solutions of iodine and hydrogen peroxide are mixed, the slow formation of iodate results.

$$I_2 + 5H_2O_2 = 2H^+ + 2IO_3^- + 4H_2O$$

The rate has been measured at 0° by Liebhafsky and Bray [*J. Am. Chem. Soc.*, **53**, 2074 (1931)]. Although the rate is, under some conditions, independent of the concentration of H_2O_2 and IO_3^-, it is complicated in that if iodate is not present initially, there is a long induction period; and, furthermore, the rate does depend somewhat on both the concentration of peroxide and that of iodate. Under some conditions, the rate of disappearance of iodine is given by

$$-\frac{d(I_2)}{dt} = k_1(I_2) - k_2(H^+)(I^-)(HIO)$$

This is the rate expression for the hydrolysis of iodine; the peroxide does not, as one might wish to believe at first sight, react directly and rapidly with the HIO to produce iodate. The tentative mechanism is the more complicated one given by the following equations:

$$\begin{aligned} I_2 + H_2O &= H^+ + I^- + HIO \\ IO_3^- + I^- + 2H^+ &= H_2I_2O_3 \\ H_2I_2O_3 + H_2O_2 &= 2HIO_2 + H_2O \\ HIO_2 + HIO &= H_2I_2O_3 \\ HIO_2 + H_2O_2 &= IO_3^- + H^+ + H_2O \end{aligned}$$

As a result of his study of this reaction and others, Liebhafsky concluded that k_1 is greater than 0.6 at 25°, and is not equal to 0.25, as Abel reported; he could not, unfortunately, put an upper limit on k_1.

The catalytic decomposition of hydrogen peroxide by hydrobromic acid is an example of a reaction that is not attended by the many complications shown by the peroxide-iodine reaction. As a result of a careful study of the hydrobromic acid catalyses [Bray and Livingston, *J. Am. Chem. Soc.*, **45**, 1251 (1923); **45**, 2048 (1923); **50**, 1654 (1928)], the mechanism has been established. The main reactions are

$$H_2O_2 + 2H^+ + 2Br^- = Br_2 + 2H_2O$$
$$H_2O_2 + Br_2 = O_2 + 2H^+ + 2Br^-$$

the second reaction being quite rapid. At the steady state, that is, at the state where the rate of disappearance of H_2O_2 is the same for the two reactions, the rate equation is

$$-\frac{d(H_2O_2)}{dt} = k(H_2O_2)(H^+)(Br^-)$$

At some distance from the steady state, the rate of formation and the rate of disappearance of bromine are given by

$$\frac{d(Br_2)}{dt} = k_1(H_2O_2)(H^+)(Br^-)$$
$$-\frac{d(Br_2)}{dt} = \frac{k_2(H_2O_2)(Br_2)}{(H^+)(Br^-)}$$

When, at the steady state, these two rates are equal,

$$\frac{(Br_2)}{(H^+)^2(Br^-)^2} = \frac{k_1}{k_2} = R, \text{ a constant}$$

R is known as the *steady state* function. The rate of reduction of bromine is quite rapid, and a flow method was used to measure it. If (H^+) and (Br^-) are not the concentrations of these ions but are their activities, then $k_1 = 0.022$, $k_2 = 0.018$, and $R = 1.2$ to 1.7 at 25°. Time is expressed in minutes and concentrations in moles per liter of solution.

The form of the two rate equations suggests the following mechanism:

$$H_2O_2 + H^+ + Br^- = HBrO + H_2O_2$$
$$H_2O_2 + HBrO = H^+ + Br^- + H_2O + O_2$$

The rate equation corresponding to the second reaction would be

$$-\frac{d(H_2O_2)}{dt} = k'(H_2O_2)(HBrO)$$

but when the rapid reversible reaction,

$$Br_2 + H_2O = H^+ + Br^- + HBrO$$

is taken into consideration,

$$-\frac{d(H_2O_2)}{dt} = -\frac{d(Br_2)}{dt} = \frac{k_2(H_2O_2)(Br_2)}{(H^+)(Br^-)}$$

and this is the same as the rate equation established experimentally.

This reaction is of importance not only as a special case, but also for the suggestion that all catalytic reactions may consist of a set of compensating reactions. Thus, although the mechanism of the catalytic decomposition of hydrogen peroxide by manganese dioxide has not been investigated, the fact that acid solutions containing $MnO_2(s)$ oxidize, and neutral solutions of Mn^{++} or $Mn(OH)_2$ reduce H_2O_2, suggests that these compensating reactions are involved in the catalytic action of MnO_2 on H_2O_2. Other couples have been found which bring about the catalytic decomposition of H_2O_2. The mechanisms are frequently more complicated than those described above. As examples of these couples we may cite

Fe^{+++}, FeO_2H^{++}, or $FeO_4^{=}$	[Bohnson and Robertson, *J. Am. Chem. Soc.*, **45**, 2493 (1923); Bray, *Chem. Rev.*, **10**, 161 (1932)]
Cr^{+++}, $Cr_2O_7^{=}$, or $CrO_4^{=}$	[Spitalsky, *Z. anorg. Chem.*, **69**, 179 (1910). *et ante*]
VO^{++}, HVO_3, and HVO_4	[Yost, unpublished experiments]

It has been possible to consider here only a few of the many reactions in which hydrogen peroxide takes part. There are a large number of isolated cases of oxidation or reduction which are of interest in connection with preparations or analysis (*e. g.*, aqueous solutions of ClO_2 may be reduced to chlorite, ClO_2^-, by $BaO_2(s)$; metallic and lower-valence forms of rhenium are readily oxidized to perrhenate ion, ReO_4^-, by H_2O_2 solutions) about which information is best sought in the handbooks or the chemical literature. The reactions described above serve as important examples of the dual role played by hydrogen peroxide; it can act readily as either an oxidizing agent or a reducing agent.

Metallic peroxides and superoxides

The two most common peroxides of metals are sodium peroxide, Na_2O_2, and barium peroxide, BaO_2. The former was, at one time, manufactured by allowing dry air to pass over metallic sodium, but the present-day method makes use of a two-step process in which the following reactions take place:

$$2Na \text{ (mixed with } Na_2O) + \tfrac{1}{2}O_2 = Na_2O \quad \text{(First step)}$$
$$Na_2O + \tfrac{1}{2}O_2 = Na_2O_2 \quad \text{(Second step)}$$

It is noteworthy that the second reaction has a very strong tendency to take place; decomposition of Na_2O_2 into Na_2O and oxygen does not take place until the temperature is above the melting point (460°; b.p. 660°). In neither step is the temperature very high. The resulting compound is orange-yellow in color and dissolves in water with the evolution of considerable heat and the formation of extensively hydrolyzed solutions of sodium peroxide. Since the first ionization constant of H_2O_2 is [Kargin, *Z. anorg. Chem.*, **183**, 77 (1929)]

$$\frac{(H^+)(HO_2^-)}{(H_2O_2)} = 1.55 \times 10^{-12} \text{ at } 20°$$

it is to be expected that the second ionization constant would be still smaller (10^{-25}), and that, accordingly, the hydrolysis of Na_2O_2 would be extensive. The solutions are strongly alkaline and are strong oxidizing agents, $E°$ for $3OH^- = HO_2^- + H_2O + 2E^-$ being -0.87 volt [Latimer, *Oxidation Potentials*, p. 39].

Sodium peroxide finds a number of uses as an oxidizing agent and as a starting material for the preparation of hydrogen peroxide.

Barium peroxide, a faintly yellow-colored compound, is formed when BaO is heated in air. The reaction is reversible [Hildebrand, *J. Am. Chem. Soc.*, **34**, 246 (1912)]:

$$BaO + \tfrac{1}{2}O_2 = Ba_2O_2$$

and, before methods for the fractional distillation of air were developed, it was utilized in the commercial preparation of oxygen. Barium peroxide may be used for the preparation of chlorites, $Ba(ClO_2)_2$, by reacting an aqueous solution of ClO_2 with solid BaO_2 [Smith, Pitzer, and Latimer, *J. Am. Chem. Soc.*, **59**, 2640 (1937)].

Less well known are lithium peroxide, Li_2O_2, strontium peroxide, SrO_2, and calcium peroxide, CaO_2. The methods of preparation in these cases consist of heating the metal or oxide in oxygen or precipitating the anhydrous peroxide from the concentrated solution of the metal ion by the addition of hydrogen peroxide [Riesenfeld and Nottebohm, *Z. anorg. Chem.*, **89**, 408 (1914)]. The peroxides do not form readily; even on heating the oxide in oxygen under pressure under the most favorable conditions (for SrO, 400° and O_2 press. of 100 kg/cm²), only about 15% yield is obtained [Fischer and Ploetze, *Z. anorg. Chem.*, **75**, 10 (1912)].

Potassium peroxide is a white to cream-colored compound which is formed when the metal dissolved in liquid ammonia is reacted with oxygen at −50° to −60° [Kraus and Parmenter, *J. Am. Chem. Soc.*, **56**, 2384 (1934)]. It is not a common substance, mainly because it reacts violently with oxygen to form the superoxide, KO_2, or a mixture of K_2O_2 and KO_2. Caesium and rubidium also show strong tendencies to form the superoxides CsO_2 and RbO_2, and, therefore, the peroxides are obtained only when the metals are reacted with oxygen under special conditions.

The superoxides KO_2, RbO_2, and CsO_2 may be prepared by treating liquid ammonia solutions of the metals with oxygen, a very pure product being obtained if the temperature is maintained at about −50° [Kraus and Parmenter, *loc. cit.*]. The product formed at higher temperatures is contaminated with some nitrite and nitrate. A better method for the preparation of the alkali superoxides consists in burning the vapors in air or oxygen; the product is obtained as a fluffy, orange-yellow powder. Sodium superoxide is not known.

Since potassium superoxide is the most common of the superoxides, its properties will serve best as examples of those of the group. KO_2 reacts with water vapor to form, rapidly, oxygen and KOH. With liquid water the reaction is

$$2KO_2 + H_2O = 2K^+ + OH^- + HO_2^- + O_2$$

With some organic compounds, such as oil, ignition and fire may result, although with others no reactions are observed under ordinary conditions.

When KO_2 is heated, reversible decomposition into oxygen and a mixture of K_2O_2 and KO_2 takes place, the solid phase becoming dark in color with loss of oxygen. Because the solid phase consists of a solid or molten solution, the oxygen pressures do not represent equilibrium pressures for a simple three-phase, two-component system [see, *e.g.*, Kraus and Whyte, *J. Am. Chem. Soc.*, **48,** 1781 (1926); Centnerszwer, *B. Acad. Polon.*, **A,** 504 (1933)].

The structure of KO_2 has been the subject of some dispute [Klein and Sodemann, *Z. anorg. Chem.*, **225,** 273 (1935)], but the difference in opinion has been resolved. The compound is paramagnetic [Neuman, *J. Chem. Phys.*, **2,** 31 (1934)], the susceptibility corresponding to one unpaired electron spin. Moreover, the crystal structure shows the potassium and superoxide ions, O_2^-, to be arranged in a simple cubic array [Helms and Klemm, *Z. anorg. Chem.*, **241,** 97 (1939)]. Accordingly, the formula KO_2 is indicated rather than the older K_2O_4. Helms and Klemm also measured the magnetic susceptibilities of the alkali superoxides, with the following results [see also Klemm and Sodomann, *loc. cit.*]. The X-ray

	KO_2	RbO_2	CsO_2
Specific susceptibility $\chi \times 10^6$:			
90°K	—	42.2	27.3
293°K	—	13.0	9.3
Bohr magnetons:			
calc. from χ at 90°K	1.97	1.89	1.91
calc. from χ at 293°K	1.84	1.89	1.89

crystal-structure studies showed the oxide having the empirical formula K_2O_3 to be a mixture of K_2O_2 and KO_2.

The following table summarizes the present information as to the simpler properties of the alkali superoxides [$Ca(O_2)_2$ is the only alkaline earth superoxide definitely established].

TABLE 108
PROPERTIES OF THE ALKALI SUPEROXIDES

Property	KO_2	RbO_2	CsO_2
Color of crystals (cold)	Yellow	Yellow	Yellow
Color of crystals (hot)	Orange	Dark orange	Reddish yellow
Color of molten material	Black	Brownish black	Black
Crystalline form	Cubic	Plates	Needles
$-\Delta H(2M + 2O_2 = 2MO_2)$ (in kilocal.)	133.74	137.6	141.46
Melting point (°C)	380°	412°	432°
Density	2.15	3.06	3.8

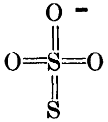
The thionic acids and their salts

Attention has already been called to the similarity between the per- or polysulfides and the peroxides. It is natural to suppose that the peroxyacids have sulfur analogues, and, indeed, this is found to be the case. But sulfur proves capable of forming the polythionic radicals, which contain more sulfur atoms bound together than there are oxygen atoms bound together in the peroxyacids.

The simple oxyacids of sulfur are H_2SO_2, sulfoxylic acid [known only as salts, $ZnSO_2$, and organic derivatives or addition products, $(C_6H_5—CH_2)_2SO_2$ and $R—CH(OH)(OSONa)$], $H_2S_2O_4$, hyposulfurous acid (the salts are well known), H_2SO_3, sulfurous acid, and H_2SO_4, sulfuric acid. When sulfur dioxide is passed into an aqueous suspension of MnO_2, there is formed $H_2S_2O_6$, dithionic acid, a sulfur acid which resembles more the simple oxyacids than the thio acids which are to be discussed. The thio acids are more complicated than the simple oxyacids and fall, with respect to their chemical properties and structures, into a class by themselves.

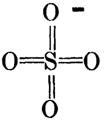
Thiosulfuric acid

When sodium sulfite solutions are heated with elementary sulfur, the familiar sodium thiosulfate, $Na_2S_2O_3$, is formed and can be crystallized out in very pure state. In neutral solutions, thiosulfates are quite stable. The structure of the thiosulfate ion, $S_2O_3^=$, has received considerable attention and is now fairly well established to be the following:



$$O{=}\overset{\overset{\displaystyle O^{-}}{\|}}{\underset{\underset{\displaystyle S}{\|}}{S}}{=}O$$

Thiosulfate ion



$$O{=}\overset{\overset{\displaystyle O^{-}}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{=}O$$

Sulfate ion

The close relation between the thiosulfate and sulfate ions is clearly brought out by these structural formulas. Evidence for this structure of thiosulfate ion is found in the reaction

$$SO_3^{=} + S = S_2O_3^{=}$$

and most strikingly in the fact that radioactive sulfur may be added to sulfite and then removed (by acidifying the thiosulfate formed), the resulting sulfite containing little or no radioactive sulfur [Libby, *J. Am. Chem. Soc.*, **59,** 2474 (1937); Anderson, *Z. phys. Chem.*, **B32,** 237 (1936)].

$$SO_3^{=} + S^* = SS^*O_3^{=}$$
$$SS^*O_3^{=} + 2H^* = H_2SO_3 + S^*$$

The symbol S* stands for radioactive sulfur. This experiment proves that the two sulfur atoms in $S_2O_3^{=}$ are not equivalent. If they had been equivalent, then half of the radioactive sulfur would have remained in the sulfite and the other half precipitated as elementary sulfur. The structure given above for the thiosulfate ion is not, of course, the only one that can be written down having two nonequivalent sulfur atoms; but, taken together with our general notions of atomic structure and the qualitative nature of the reactions of thiosulfate, it is regarded as the most probable one. Looked at from the rather vague notions of valence, one would say that the central sulfur atom is a sulfate sulfur, the outer one a sulfide sulfur. The two sulfur atoms, notwithstanding the fact that they are bound together, are not regarded as forming a persulfide group.

The alkali and alkaline earth thiosulfates are quite soluble ($3K_2S_2O_3 \cdot 5H_2O$, 165 g/100 g H_2O at 25°, 155.4 g/100 g H_2O at 20°; $Na_2S_2O_3 \cdot 5H_2O$, 74.7 g/100 g H_2O at 0°, 301.5 g/100 g H_2O at 60°. $Na_2S_2O_3 \cdot 5H_2O$ melts at 48.4°, and the liquid may then be supercooled). When sufficiently concentrated, at 80° to 141°, the calcium salt slowly and reversibly decomposes according to the equation [Bichowsky, *J. Am. Chem. Soc.*, **45,** 2225 (1923)],

$$CaS_2O_3(aq) + H_2O = CaSO_4 \cdot 2H_2O(s) + S(s)$$

From the equilibrium measurements and other known data, the free energy of formation of $S_2O_3^{=}$ has been determined to be $\Delta F^{\circ}_{298} = -124{,}800$ cal/mole. (Latimer, *Oxidation Potentials*, p. 67, believes that the correct value is nearer −124,000 cal/mole.)

Thiosulfate ion forms complex ions with several elements, the most common example being that of the complex silver ion $Ag(S_2O_3)_2$. This complex ion is so stable that AgCl, AgBr, and even AgI will dissolve in a sodium thiosulfate solution, and this fact is utilized in photography, the unaltered AgBr being dissolved out of the gelatin emulsion. Complex ions are also formed with Pb^{++}, Hg^{++}, Bi^{+++}, Cu^{+}, Cd^{++}, and trivalent arsenic and antimony. Several of the complex ions have a sweet taste. If a solution containing a heavy metal ion (Ag^+, Pb^{++}, or Cu^{++}) is heated, sulfides, sulfates, and some trithionate are formed.

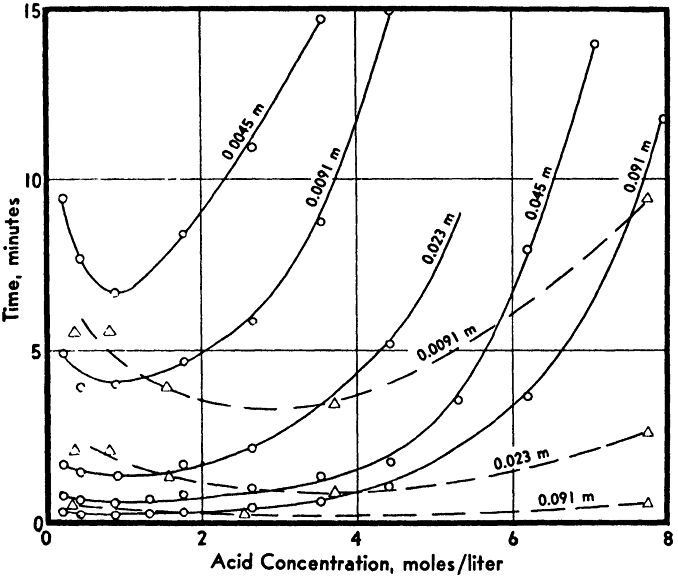


Fig. 72. The Time of Appearance of Sulfur in Acidified Sodium Thiosulfate Solutions of Various Thiosulfate and Acid Concentrations. Solid lines are for hydrochloric acid solutions, dashed lines for phosphoric acid solutions. The concentration of thiosulfate is indicated on each curve.

The treatment of thiosulfate with mild or slowly reacting oxidizing agents (I_2, $S_2O_8^{=}$) results in the formation of tetrathionate. Thus,

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-$$

a reaction much used in the volumetric determination of iodine. With stronger or more reactive oxidizing agents (I_2 in alkaline solutions, Br_2, Cl_2, MnO_4^-), sulfate is the end product.

If a sodium thiosulfate solution is treated with a dilute, strong acid, sulfur precipitates out after a short time,

$$S_2O_3^{=} + 2H^+ = H_2SO_3 + S$$

If a concentrated acid is added in such an amount that the final solution contains a high concentration of acid, sulfur appears after a much longer time; and, indeed, if the solution is about 10 or 12 n in HCl, no sulfur at all appears for some hours. The effect of acid concentration is clearly shown in Fig. 72. The results are due to Bassett and Durant [*J. Chem. Soc.*, 1401 (1927)]. The strongly acid solutions are excellent reducing agents; even methylene blue and indigo are discolored by them, and iodine is reduced as readily as by the neutral thiosulfate. It was suggested by Bassett and Durant that the acid solutions contain the compound $H_2S_4O_5$ formed in the reaction,

$$2S_2O_3^= + 2H^+ = S_4O_5^= + H_2O$$

and that at high acid concentrations and low H_2O activities, this reaction is favored over that producing sulfur and sulfurous acid. However, the evidence for the existence of $H_2S_4O_5$ was indirect and has been questioned by Janickis [*Z. anorg. Chem.*, **234**, 193 (1937)], who believes that the undissociated $H_2S_2O_3$ itself is stable. Janickis added 5 ml of 2 n $Na_2S_2O_3$ solution to 90 ml of concentrated HCl cooled to −20°. After the precipitate of NaCl had settled, the solution was warmed to 0° and diluted with concentrated HCl to 100 ml. The solutions remained clear and colorless at 0° for about eight hours. A series of analyses gave the following compositions as a function of the time after the addition of the sodium thiosulfate. The row labeled "$H_2S_2O_3$" includes any substance which reduces methylene blue. It will be noted that there is a steady decomposition during which increasing amounts of the higher polythionic acids are formed, and it is with these acids and their salts that the remainder of this section is concerned.

Compositions, in 100 ml of Solution*

Time after preparation	15 min.		1 hr.		2 hr.		4 hr.		8 hr. 20 min.	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
$H_2S_2O_3$	6.84	13.68	5.86	11.36	5.05	10.10	4.22	8.44	3.36	6.72
$SO_2 + H_2S$.	2.46	2.46	3.61	3.61	4.08	4.08	4.51	4.51	4.91	4.91
Polythionic acids . . .	0.62	4.52	0.48	5.67	0.45	6.35	0.68	0.68	0.94	9.40

* In column (a) are given the amounts in millimoles; in column (b) are given the amounts of sulfur in milliatomic weights contained in the compounds. The solutions remained clear, but the presence of colloidal sulfur is not excluded; the amounts of sulfur under (b) for polythionic acids may well include any colloidal sulfur.

The polythionic acids

The polythionates have the general formula $S_nO_6^=$, with *n* greater than two, and are characterized by having three or more sulfur atoms bound together. Their reactions with each other and with other reagents are, for the most part, complicated, to say the least. Although a number of investigations have been made, the nature and mechanisms of the reactions are not always clear. In fact, it may be safely said that the chemistry of the thionates and polysulfides, like that of the peroxides, falls in a class by itself, and as such its nature and applications have received insufficient attention to resolve all the problems that have arisen. The literature up to 1926 on the polythionates is reviewed in an excellent article by Kurtenacker in Abegg and Auerbach, *Handbuch der Anorganischen Chemie,* Vol. IV, Part 1, p. 543, 1927; for more recent work, see the numerous articles by Kurtenacker and co-workers in the *Zeitschrift für anorganische und allgemeine Chemie.*

When sodium thiosulfate is added to cooled hydrochloric acid solutions in which a small amount of arsenious oxide has been dissolved, much higher yields of polythionic acids are obtained than when arsenite is absent. The relative proportions of the various thionic acids formed depend upon the concentration of the acid and the amount of arsenious oxide used; a higher acid concentration leads to more of the higher thionic acids, while a higher arsenite concentration leads to more of the lower acids. Results of typical experiments are given below [Kurtenacker and Matejka, *Z. anorg. Chem.*, **229,** 19 (1936)]. The value of n was determined by utilizing the reactions,

Reactants				Product $S_nO_6^=$, Value of n
$Na_2S_2O_3 \cdot 5H_2O$	As_2O_3	Conc. HCl	H_2O	
30 g	0.2 g	40 ml	30 ml	5.5
30	.2	50	20	7.2
30	.2	70	0	8.2
30*	.2	70	0	10.0
30*	1.5	70	0	5.3

* Anhydrous salt.

$$S_nO_6^= + S^= = (n-3)S + 2S_2O_3^=$$
$$S_nO_6^= + S^= + (n-3)SO_3^= = (n-1)S_2O_3^=$$

which are characteristic of all the polythionic acids. In the first case sodium sulfide is added to the solution, and in the second, sulfide plus sulfite. The resulting thiosulfate is titrated with iodine. These experiments indicate the existence of $S_{10}O_6^=$ if the assumption is made that all the sulfur is bound in a polythionic acid. However, the assumption is probably not justified, since colloidal sulfur interferes in the second reaction by forming thiosulfate with the sulfite. The highest polythionate which has been isolated and characterized is the hexathionate.

The sodium and potassium thionates are the ones usually prepared, and they are soluble, crystalline salts. Polythionic acids are strong, dibasic acids, no alkali acid salts being known, although an acid tetra- and pentathionate of zinc have been prepared; normal salts of cobalt, nickel, zinc, copper, bismuth, and manganese have been prepared also [Deines and Christoph, *Z. anorg. Chem.*, **213,** 209 (1933)]. In Table 109 are given the solubilities of some polythionates in water. The heavy metal salts are soluble in alcohol, acetone, and other organic solvents.

Table 109
SOLUBILITIES OF THE POLYTHIONATES
(g anhydrous salt/100 g solution)

	0°	20°
$Na_2S_3O_6{\cdot}3H_2O$	37.8	52.9
$Na_2S_4O_6{\cdot}2H_2O$	41.3	50.4
$Na_2S_5O_6{\cdot}2H_2O$	32.9	52.0
$K_2S_3O_6$	8.1	18.4
$K_2S_4O_6$	12.6	23.2
$K_2S_5O_6$	15.5	24.8
BaS_4O_6	26.6	32.3

An elaborate scheme of analysis for the separate determination, to a few per cent, of S, $SO_3^{=}$, $S^{=}$, $SO_4^{=}$, $S_2O_3^{=}$, $S_3O_6^{=}$, $S_4O_6^{=}$, $S_5O_6^{=}$, and $S_6O_6^{=}$ in mixtures has been worked out by Kurtenacker and his co-workers [*Z. anorg. Chem.*, **166,** 187 (1927); Kurtenacker, *Analytische Chemie der Sauerstoffsauren des Schwefels*, Stuttgart, 1938]. Some of the reactions utilized which are common to the whole group are given here; other more specific reactions are given in the discussions of the individual compounds.

All of the polythionates react with cyanide, slowly at room temperature in neutral solution but rapidly and quantitatively in hot alkaline solution.

$$S_3O_6^{=} + CN^- + H_2O = SO_4^{=} + CNS^- + H_2SO_3$$
$$S_4O_6^{=} + CN^- + H_2O = S_2O_3^{=} + SO_4^{=} + CNS^- + 2H^+$$
$$S_5O_6^{=} + 2CN^- + H_2O = S_2O_3^{=} + SO_4^{=} + 2CNS^- + 2H^+$$

Another general reaction of the polythionates is that with $HgCl_2$ in a solution heated to 70°.

$$2S_nO_6^{=} + 3HgCl_2 + 4H_2O = Hg_3S_2Cl_2(s) + 4SO_4^{=} + 4Cl^- + 8H^+ + (2n - 6)S$$

Thiosulfates also react with $HgCl_2$, hence care must be taken in using the reaction in analyses.

$$2S_2O_3^{=} + 3HgCl_2 + 2H_2O = Hg_3S_2Cl_2(s) + 2SO_4^{=} + 4Cl^- + 4H^+$$

The stabilities of the alkali polythionates in water solution have been investigated many times, and some general statements as to their decomposition may be made. In strongly acid solution, all the salts decompose rapidly, the tri- and tetrathionate mainly according to the equation

$$S_nO_6^{=} = (n - 2)S + SO_2 + SO_4^{=}$$

and the penta- and hexathionate according to the equation

$$2S_nO_6 + 4H^+ = (2n - 5)S + 5SO_2 + 2H_2O$$

The tetra- and pentathionate are much more sensitive than trithionate to hydroxyl ion, but are much more stable than trithionate in acid solution. These relationships are shown in a more quantitative way by the above rough plot (Fig. 73) of the decomposition rates, starting with solutions of single pure salts [Kurtenacker, Mutschin, and Stastny, *Z. anorg. Chem.*, **224**, 399 (1935); see this article also for a discussion of the primary products]. The rate constants are given as a function of *pH*; all runs were at 50°. The $pK = -\log_{10} k$, where

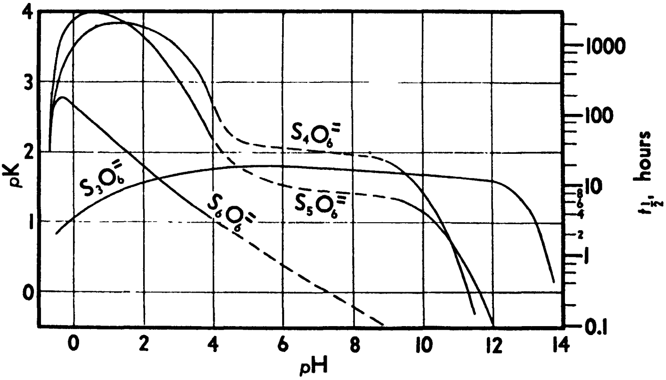


Fig. 73. The Decomposition of Polythionates at 50°C. $k = 1/t \log [a/(a - x)]$, where a = initial concentration, x = concentration at time t. $pK = -\log_{10} k$. $t_{1/2}$ = time in hours to 50% decomposition.

$$k = \frac{1}{t} \log \left(\frac{a}{a - x}\right)$$

a is the amount of constituent initially present, and $a - x$ is the amount present at the time t. The decomposition products are numerous, including other polythionic acids, thiosulfate, sulfite, sulfate, and sulfur. Figs.

74, 75, and 76 indicate the relative amounts of the various constituents; the probable initial products are discussed in the succeeding sections. Decomposition in mixtures of the various salts is even more complicated, but some idea of the process may be gained from Figs. 77 and 78.

Trithionate

This salt is best prepared by the reaction of SO_2 with thiosulfate. Finely powdered $Na_2S_2O_3 \cdot 5H_2O$ is mixed with a cooled, saturated solution of SO_2 containing a little arsenious oxide. When additional SO_2 gas is passed into the mixture, the thiosulfate goes into solution and $Na_2S_4O_6 \cdot 2H_2O$ precipitates out. After the addition of sufficient SO_2, the tetrathionate is filtered off, and the more soluble $Na_2S_3O_6$ is precipitated by adding alcohol and cooling in an ice-salt bath. The salts are purified by recrystallization from water or acetic acid solution and are dried in a dessicator.

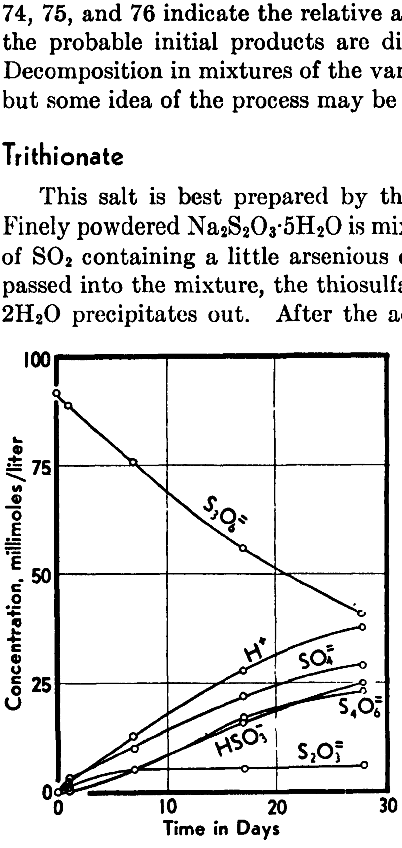
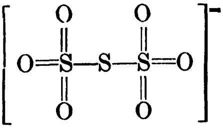


Fig. 74. The Decomposition of $K_2S_3O_6$ in Water.

Potassium trithionate is the only polythionate whose structure has been determined by X-ray crystal-structure methods [Zachariasen, *Phys. Rev.*, **37**, 1295 (1931)]; the trithionate ion may be written



$$\left[\begin{matrix} & O & & O & \\ & \| & & \| & \\ O= & S & -S- & S & =O \\ & \| & & \| & \\ & O & & O & \end{matrix}\right]^{=}$$

the two like sulfur atoms having a tetrahedron of three oxygen atoms and one sulfur atom about them. The sulfur atom is common to both tetrahedra, and the S—S—S angle is about 100°.

Sodium trithionate hydrolyzes slowly in weakly acid to weakly basic solutions first into thiosulfate and sulfate.

$$S_3O_6^= + H_2O = S_2O_3^= + SO_4^= + 2H^+$$

This reaction is followed by the more rapid reaction,

$$S_2O_3^= + S_3O_6^= + 2H^+ = S_4O_6^= + SO_3H^- + H^+$$

and various other side reactions. In strongly alkaline solutions, the main reaction is

$$2S_3O_6^= + 6OH^- = S_2O_3^= + 4SO_3^= + 3H_2O$$

Neutral solutions hydrolyze only slowly; the experiments of Kurtenacker on the decomposition rates and products are shown graphically in Fig. 74.

When Cu^{++} is added to an acid trithionate solution and the solution heated to 70°, the following reaction results:

$$2H_2O + S_3O_6^= + Cu^{++} = CuS + 2SO_4^= + 4H^+$$

Neither the tetra- nor the pentathionate reacts with Cu^{++} at 70°, and the reaction is useful for the detection of trithionate. Trithionate does not react with sulfite in neutral or weakly acid solution.

Tetrathionate

Sodium tetrathionate is obtained as a by-product in the preparation of the trithionate described above. A more common method of preparation is by the oxidation of thiosulfate with iodine [Kurtenacker and Fritsch, *Z. anorg. Chem.*, **121**, 335 (1922)]. Dry sodium tetrathionate is quite stable. Its structure is not known, but by analogy with potassium peroxydisulfate, $K_2S_2O_8$, whose structure has been determined [Zachariasen, *Phys. Rev.*, **37**, 1295 (1931)], it is probable that the four sulfur atoms are bound together in a chain; each end sulfur atom would have a tetrahedral grouping of three oxygen atoms and a sulfur about it, and the two tetrahedra would be joined through the corner sulfur atoms, the S—S—S angles being about 100°, as in the trithionate ion.

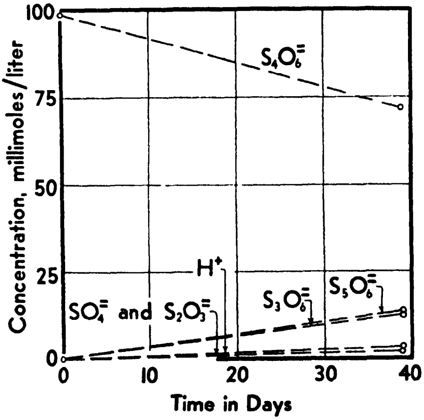


Fig. 75. The Decomposition of $Na_2S_4O_6$ in Water.

In neutral or weakly acid solutions, tetrathionate ion decomposes slowly,

$$2S_4O_6^= = S_3O_6^= + S_5O_6^=$$

in weakly alkaline solution it hydrolyzes,

$$4S_4O_6^= + 6OH^- = 5S_2O_3^= + 2S_3O_6^= + 3H_2O$$

as well as in strongly alkaline solution, the reaction in this case being,

$$2S_4O_6^= + 6OH^- = 3S_2O_3^= + 2SO_3^= + 3H_2O$$

The products of the hydrolysis in neutral solution are shown in Fig. 75.

Unlike trithionate, the tetra- and pentathionates in neutral or weakly acid solutions react with sulfites. In neutral solutions, the reactions are fairly straightforward and are [Foerster and Centner, *Z. anorg., Chem.,* **157,** 45 (1926)]

$$S_4O_6^= + SO_3^= = S_3O_6^= + S_2O_3^=$$

$$-\frac{d(S_4O_6^=)}{dt} = k_4(S_4O_6^=)(SO_3^=), \qquad k_4 = 0.0103/\text{mole min at } 0^\circ$$

$$S_5O_6^= + SO_3^= = S_4O_6^= + S_2O_3^=$$

$$-\frac{d(S_5O_6^=)}{dt} = k_5(S_5O_6^=)(SO_3^=), \qquad k_5 = 0.233/\text{mole min at } 0^\circ$$

The second reaction is followed by the first, much slower reaction. In weakly acid solutions, that is, in HSO_3^- solutions, the reactions are much slower, owing apparently to the fact that only $SO_3^=$, and not HSO_3^-, is reactive. Some sulfate is formed in the acid solutions. There is some evidence for believing that the reactions are reversible, the equilibrium lying almost completely to the right in neutral solution and less so in acid solution, as is to be expected by virtue of the weakly acid character of HSO_3^-. It is to be noted, however, that the slowness of the reactions with HSO_3^- may and probably does result in failure to reach equilibrium, since other side reactions can change the concentrations of the reactants and products at rates greater than those of the reactions considered.

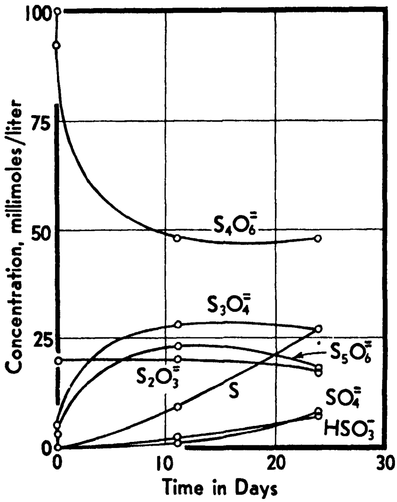


Fig. 76. **The Decomposition of $Na_2S_4O_6$ + $Na_2S_2O_3$ in Water.**

Pentathionate and hexathionate

The reaction between sodium thiosulfate and an acid solution of arsenious acid is the best method for the preparation of fairly large quantities of sodium penta- and hexathionate; the general features of this reaction have already been discussed. For the best yield of the pentathionate, 125 g $Na_2S_2O_3 \cdot 5H_2O$ is dissolved in 150 ml H_2O, and 2.5 g As_2O_3, dissolved in as little alkali as possible, added. Then the solution is cooled to −10°, and 200 ml of cooled, concentrated HCl is added. A precipitate of NaCl is quickly filtered off, and the filtrate is allowed to stand overnight. After a precipitate of As_2S_3 is filtered off, the solution is concentrated to a colorless to light-yellow oily liquid of specific gravity 1.6 by evaporation in a vacuum at 35–40°. The addition of alcohol and an acetic acid solution of potassium acetate causes the sodium pentathionate to precipitate. It may be purified by recrystallization [Kurtenacker and Fluss, *Z. anorg. Chem.*, **210,** 125 (1933)]. The preparation of sodium hexathionate is similar, except that 400 ml of concentrated HCl is used. The pentathionate formed is less soluble and is precipitated first; further evaporation causes the hexathionate to precipitate [Kurtenacker and Matejka, *Z. anorg. Chem.*, **229,** 19 (1936)]. It is reported that a pure $H_2S_5O_6$ solution results from passing a dry mixture of two moles of H_2S to one mole of SO_2 into water [Deines and Grassmann, *Z. anorg. Chem.*, **220,** 337 (1934)]. Potassium hexathionate may be prepared in another way by the addition of a 1:3 mole mixture of KNO_2 and $K_2S_2O_3$ to a cooled solution of 8 n HCl [Weitz and Achterberg, *Ber.*, **61,** 399 (1928)].

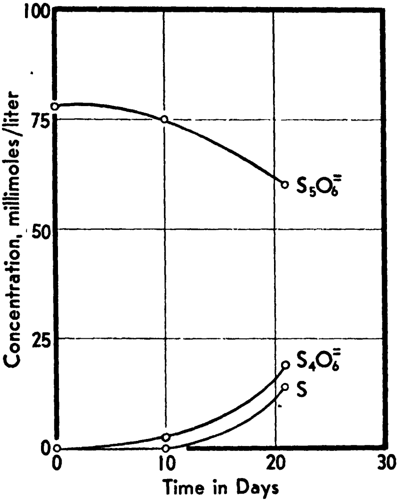


Fig. 77. The Decomposition of $K_2S_6O_6$ in Water.

In nearly neutral or weakly acid solution, the pentathionate ion decomposes into sulfur and tetrathionate.

$$S_5O_6^{=} = S_4O_6^{=} + S$$

A precipitate of sulfur results immediately on the addition of a drop of base to a solution of a pentathionate; this was formerly regarded as a distinctive test for pentathionate, but it is not known that hexathionate undergoes the same reaction. The pentathionate ion in alkaline solution of *pH* 8.9 hydrolyzes at a measurable rate to thiosulfate.

$$2S_5O_6^{=} + 6OH^- = 5S_2O_3^{=} + 3H_2O$$

The initial reactions are followed by various side reactions, as is usually the case in the decomposition of the polythionates. The hexathionate ion decomposes in alkaline, neutral, and not too strongly acid solutions in a relatively clean reaction,

$$S_6O_6^{=} = S + S_5O_6^{=}$$

Since the existence of hexathionic acid was in doubt until about 1934, less is known of its properties than of those of the other polythionic acids.

In general, its reactions are similar to those of pentathionic acid, and hexathionate has probably been present in many supposedly pure pentathionate solutions.

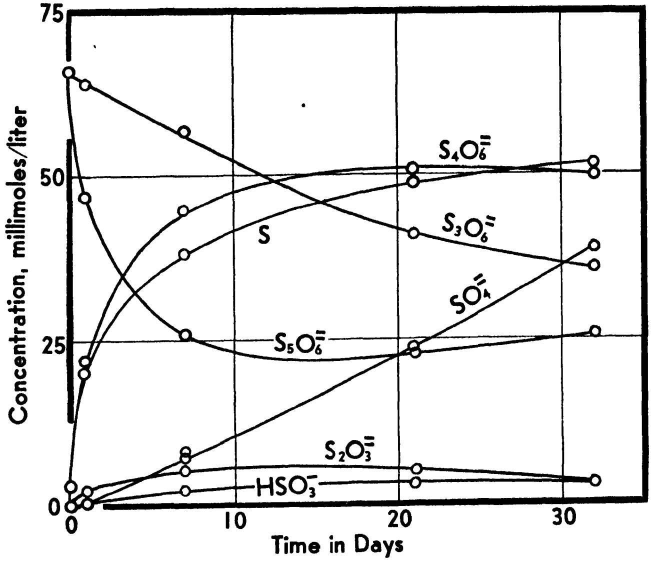


Fig. 78. The Decomposition of $K_2S_3O_6 + K_2S_5O_6$ in Water.

Wackenroder's liquid

When H_2S is passed (usually slowly and periodically) into a solution of H_2SO_3, a milky solution results which contains colloidal sulfur, hydrogen sulfide, thiosulfate, sulfite, and considerable quantities of polythionic acids; this solution is known as Wackenroder's liquid. Historically, the polythionates were first known through a study of this liquid. The relative amounts of the various constituents vary markedly according to the exact method of preparation; the ratio of penta- to tetrathionate may vary from 1:6 to 5:6, for example. A mixture of similar complexity is formed by the hydrolysis of sulfur monochloride. This is to be expected, as the hydrolysis may be formally written:

$$S_2Cl_2 + 2H_2O = SO_2 + H_2S + 2HCl$$

and the ingredients of Wackenroder's liquid would be present. This hydrolysis, and especially the reaction between H_2S and SO_2, have been extensively used for the preparation of polythionic acids, although better methods are now available for the individual salts.

In spite of numerous investigations dating from 1850, not a single feature of the mechanism of reaction between H_2S and SO_2 can be said to be firmly established. The situation is so confused that to undertake a discussion of the many proposed mechanisms would only lead to more confusion. However, one recent investigation has presented a proposed mechanism that warrants presentation, although some facts remain unexplained. Stamm and Goehring [*Ber.* **71B,** 2212 (1938); *Z. anorg. Chem.*, **242,** 413 (1939)] prepared $CH_3OSSOCH_3$ from S_2Cl_2 and CH_3ONa in anhydrous ether. On hydrolysis of this ester, a solution is obtained that was shown to exhibit fairly strong oxidizing power immediately after the hydrolysis (I^- was oxidized). Investigation showed that subsequently all the products found in Wackenroder's liquid were produced in the solution. The initial intermediate which acted as an oxidizing agent could logically be assumed to be $H_2S_2O_2$ with one hydroxyl group on each sulfur. Evidence for this structure is found in the structure of the ester that was derived from a study of the Raman spectra and the method of formation from S_2Cl_2, whose structure has been established by electron diffraction. Measurements of the rates of formation of the various constituents gave support to the following postulated mechanism:

Primarily,

$$\begin{aligned} H_2S + SO_2 &= H_2S_2O_2 \\ H_2S_2O_2 + H_2S &= 3S + 2H_2O \\ H_2S_2O_2 + 2H_2SO_3 &= H_2S_4O_6 + 2H_2O \end{aligned}$$

Secondarily,

$$\begin{aligned} H_2S_4O_6 + H_2SO_3 &= H_2S_3O_6 + H_2S_2O_3 \\ S + H_2SO_3 &= H_2S_2O_3 \\ H_2S_4O_6 + H_2S &= S + 2H_2S_2O_3 \\ H_2S_2O_2 + 2H_2S_2O_3 &= H_2S_6O_6 + 2H_2O \\ H_2S_6O_6 &= H_2S_5O_6 + S \end{aligned}$$

and other reactions of the polythionates.

This mechanism seems to be the best-supported one yet advanced. According to it, tetrathionic acid is the first polythionic acid formed; it is consequently difficult to explain the result of Deines and Grassmann [*Z. anorg. Chem.*, **220,** 337 (1934)] that pentathionic acid is formed quantitatively by passing a dry 2:1 molar mixture of H_2S and SO_2 into water. The investigations are, however, an important step toward a modern treatment of a difficult problem.

APPENDIX A

Bibliography of Reference Books

The following bibliography contains the titles of books which are frequently referred to in the text by author and title only. Included in the list are several books which are not specifically referred to in the present volume but which were found to be of special value for gaining clarity on many questions of theory or fact. Chemistry, like the few other fundamental sciences, is subject to continual increase in factual material and change in theoretical framework, and it is, therefore, suggested that the books in the list be not regarded as so authoritative and eternally fixed that a second Roger Bacon would be required to direct attention away from them. It is true, however, that these books, or their equivalent, do present much of our best knowledge of the various phases of inorganic chemistry.

Inorganic Chemistry

Abegg, R., Fr. Auerbach, and I. Koppel, *Handbuch der Anorganischen Chemie*, Hirzel, Leipzig, 1937.

Archibald, E. H., *The Preparation of Pure Inorganic Substances*, John Wiley, New York, 1932.

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Curtis, H. A., *Fixed Nitrogen*, Chemical Catalog Co., New York, 1932.

Emeleus, H. J., and J. S. Anderson, *Modern Aspects of Inorganic Chemistry*, D. Van Nostrand, New York, 1938.

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Kurtenacker, A., *Analytische Chemie der Saurstoffsauren des Schwefels*, F. Enke, Stuttgart, 1938.

Latimer, W. M., *Oxidation Potentials*,* Prentice-Hall, New York, 1938.

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* The title of Professor Latimer's *Oxidation Potentials* suggests a chemical-thermodynamics character, but he has adopted a predominantly chemical point of view in the presentation. Since the book so admirably serves a double purpose, it is placed under two classifications in the Bibliography.

Machu, W., *Das Wasserstoffperoxyd und die Perverbindung*, Julius Springer, Berlin, 1937.

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Atomic and Molecular Structure

Dirac, P. A. M., *Principles of Quantum Mechanics*, Oxford University Press, 2nd ed., 1935.

Herzberg, G., *Molecular Spectra and Molecular Structure*, Prentice-Hall, New York, 1939.

Jevons, W., *Report on Band-Spectra of Diatomic Molecules*, the Physical Society, London, 1932.

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Millikan, R. A., *Electrons (+ and −), Protons, Photons, Neutrons, and Cosmic Rays*, University of Chicago Press, 1935.

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*See footnote on page 400.

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APPENDIX B

General Physical Constants

The following Table I contains chemically relevant values taken mainly from the 1941 list of the general (fundamental) physical constants. The 1941 list is the work of Birge [*Rev. Mod. Phys.*, **13**, 233 (1941)], and because, throughout the years, he has given such careful attention to the subject, there can be little doubt as to the current reliability of the values which he has published. [See also Benford, *Phys. Rev.*, **63**, 212 (1943); Birge, *ibid.*, **64**, 213 (1943).] It will be understood that, as a result of newer experimental data, the values are subject to periodic revision.

TABLE I
GENERAL PHYSICAL CONSTANTS

Name	Symbol	Value
Velocity of light	c	2.99776×10^{10} cm/sec
Volume of ideal gas	V_0	22.4140 liters/mole
Ice point, 0°C	T_0	273.16°K
Faraday constant	F	96,501 international coulombs/chem. equiv.
Electronic charge	e	4.8025×10^{-10} esu
Specific electronic charge	e/m	1.7592×10^{7} emu/g
Specific electronic charge	ec/m	5.2736×10^{17} esu/g
Avogadro's number	N_0	6.0228×10^{23} mole^{-1}
Planck constant	h	6.6242×10^{-27} erg. sec
Boltzmann constant	k	1.38047×10^{-16} erg/deg
Gas constant	R_0	1.98670 cal/deg/mole
International ohm	p	1.00048 absolute ohms
International ampere	q	0.99986 absolute ampere
Calorie*	J	4.1833 International Joules
Calorie*	J	4.1850 absolute Joules
Standard gravitational acceleration	g	980.665 cm/sec^2
Standard density of mercury at 0°C	ρ_{Hg}	13.59504 g/cm^3
Liter	l	1000.028 cm^3
Bohr Magneton	$\mu_0 = he/4\pi m$	0.9273×10^{-20} erg/gauss
Bohr Magneton	$\mu_0 N_0$	5585.2 erg/gauss/mole

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* Chemists' defined calorie, now in common use.

The symbols used throughout this book to designate concentrations are either defined in the text or they are used in the more modern physical chemical sense. That is, m or *f* signifies moles or formula weights per 1000 grams of solvent; the normality, *N* or n, refers to equivalents or formula weights, as the case may be, per liter of solution.

TABLE II
INTERNATIONAL ATOMIC WEIGHTS*

Element	Symbol	Atomic Number	Atomic Weight	Element	Symbol	Atomic Number	Atomic Weight
Aluminum....	Al	13	26.97	Molybdenum..	Mo	42	95.95
Antimony.....	Sb	51	121.76	Neodymium...	Nd	60	144 27
Argon........	A	18	39.944	Neon.........	Ne	10	20.183
Arsenic.......	As	33	74.91	Nickel........	Ni	28	58.69
Barium.......	Ba	56	137.36	Nitrogen......	N	7	14 008
Beryllium.....	Be	4	9.02	Osmium......	Os	76	190.2
Bismuth......	Bi	83	209.00	Oxygen.......	O	8	16 0000
Boron........	B	5	10.82	Palladium.....	Pd	46	106.7
Bromine......	Br	35	79.916	Phosphorus....	P	15	30 98
Cadmium....	Cd	48	112.41	Platinum.....	Pt	78	195.23
Calcium......	Ca	20	40 08	Potassium.....	K	19	39 096
Carbon.......	C	6	12.010	Praseodymium.	Pr	59	140 92
Cerium.......	Ce	58	140.13	Protactinium..	Pa	91	231
Cesium.......	Cs	55	132.91	Radium.......	Ra	88	226 05
Chlorine......	Cl	17	35.457	Radon........	Rn	86	222
Chromium....	Cr	24	52.01	Rhenium......	Re	75	186.31
Cobalt...... ..	Co	27	58 94	Rhodium.....	Rh	45	102 91
Columbium...	Cb	41	92.91	Rubidium.....	Rb	37	85 48
Copper.......	Cu	29	63.57	Ruthenium....	Ru	44	101.7
Dysprosium...	Dy	66	162 46	Samarium	Sm	62	150.43
Erbium.......	Er	68	167 2	Scandium.....	Sc	21	45 10
Europium.....	Eu	63	152 0	Selenium......	Se	34	78.96
Fluorine......	F	9	19.00	Silicon.......	Si	14	28 06
Gadolinium...	Gd	64	156.9	Silver.........	Ag	47	107.880
Gallium.......	Ga	31	69.72	Sodium	Na	11	22 997
Germanium...	Ge	32	72.60	Strontium.....	Sr	38	87 63
Gold........	Au	79	197.2	Sulfur........	S	16	32.06
Hafnium......	Hf	72	178 6	Tantalum.....	Ta	73	180 88
Helium.......	He	2	4.003	Tellurium.....	Te	52	127.61
Holmium....	Ho	67	164.94	Terbium......	Tb	65	159.2
Hydrogen.....	H	1	1.0080	Thallium......	Tl	81	204.39
Indium.......	In	49	114.76	Thorium......	Th	90	232.12
Iodine.......	I	53	126.92	Thulium......	Tm	69	169.4
Iridium.......	Ir	77	193.1	Tin...........	Sn	50	118.70
Iron.........	Fe	26	55.85	Titanium......	Ti	22	47.90
Krypton......	Kr	36	83 7	Tungsten......	W	74	183 92
Lanthanum...	La	57	138.92	Uranium......	U	92	238 07
Lead.........	Pb	82	207.21	Vanadium	V	23	50.95
Lithium.......	Li	3	6.940	Xenon........	Xe	54	131.3
Lutecium.....	Lu	71	174.99	Ytterbium....	Yb	70	173 04
Magnesium....	Mg	12	24.32	Yttrium......	Y	39	88.92
Manganese....	Mn	25	54.93	Zinc..........	Zn	30	65.38
Mercury......	Hg	80	200.61	Zirconium.....	Zr	40	91 22

* G. P. Baxter, *J. Am. Chem. Soc.*, **65**, 1443 (1943).

Because the basis for this table is 16.0000 for ordinary oxygen, the values are slightly different from those used and published by physicists. The basis for the physicists' tables is the isotope O^{16} = 16.00000; this refinement is essential when mass (energy) balances are being computed.

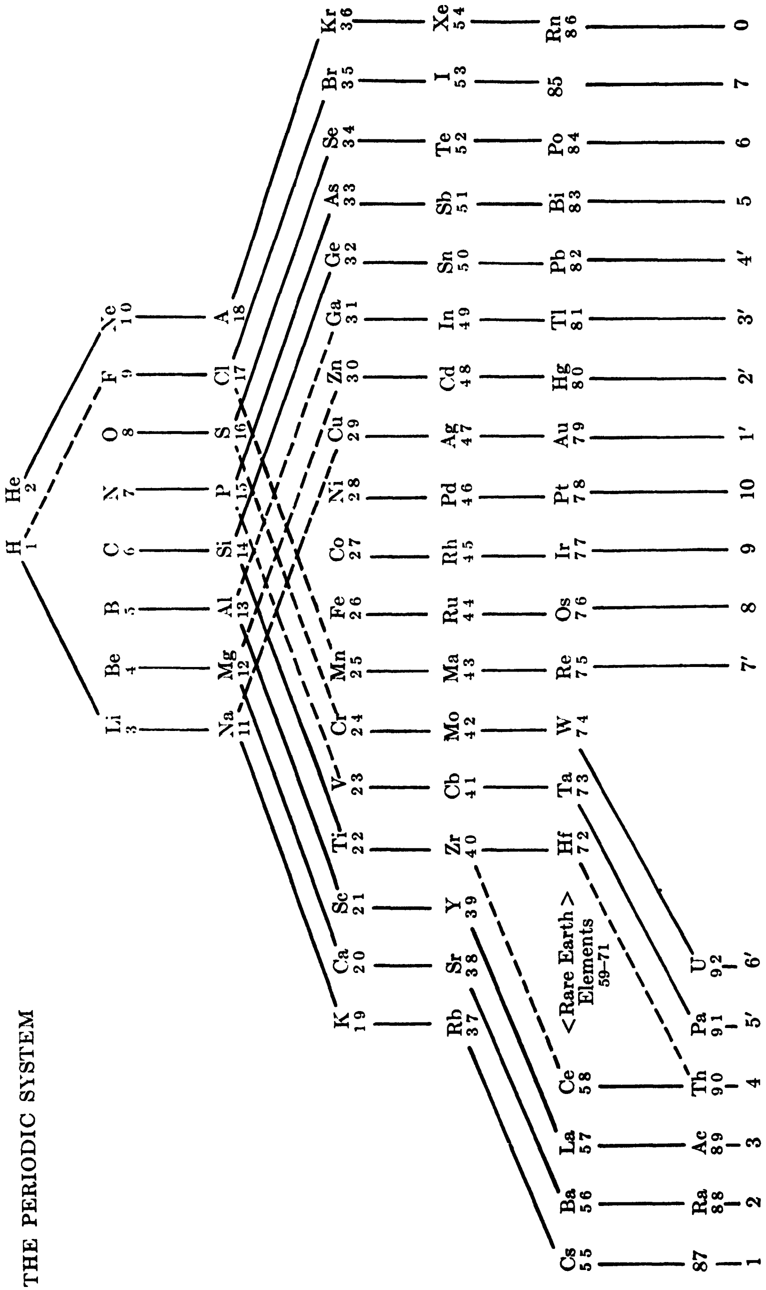
APPENDIX C

The Periodic System of the Elements

I	I′	II	II′	III	III′	IV	IV′	V	V′	VI	VI′	VII	VII′	VIII	A	B	C
H 1														He 2			
Li 3		Be 4		B 5			C 6		N 7		O 8		F 9	Ne 10			
Na 11		Mg 12		Al 13			Si 14		P 15		S 16		Cl 17	A 18			
K 19		Ca 20		Sc 21		Ti 22		V 23		Cr 24		Mn 25			Fe 26	Co 27	Ni 28
	Cu 29		Zn 30		Ga 31		Ge 32		As 33		Se 34		Br 35	Kr 36			
Rb 37		Sr 38		Y 39		Zr 40		Cb 41		Mo 42		Ma 43			Ru 44	Rh 45	Pd 46
	Ag 47		Cd 48		In 49		Sn 50		Sb 51		Te 52		I 53	Xe 54			
Cs 55		Ba 56		La See note 57													
						Hf 72		Ta 73		W 74		Re 75			Os 76	Ir 77	Pt 78
	Au 79		Hg 80		Tl 81		Pb 82		Bi 83		Po 84		— 85	Rn 86			
— 87		Ra 88		Ac 89		Th 90		Pa 91		U 92							

Following lanthanum, atomic number 57, are the *rare earth elements*. They are cerium, 58; praseodymium, 59; neodymium, 60; illinium, 61(?); samarium, 62; europium, 63; gadolinium, 64; terbium, 65; dysprosium, 66; holmium, 67; erbium, 68; thulium, 69; ytterbium, 70; lutecium, 71.

THE PERIODIC SYSTEM



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