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ATOMIC WEIGHTS

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Name	Symbol	Atomic Number	Atomic Weight *	Name	Symbol	Atomic Number	Atomic Weight *
Actinium	Ac	89	227.0	Molybdenum	Mo	42	95.95
Aluminum	Al	13				60	144.27
Americium						10	20.183
Antimony						93	(237)
Argon						28	58.69
Arsenic						41	92.91
Astatine						7	14.008
Barium						76	190.2
Berkelium							16.0000
Beryllium							106.7
Bismuth							30.98
Boron							195.23
Bromine							239)
Cadmium							210
Californium							39.096
Calcium							140.92
Carbon							147)
Cerium							231
Cesium							226.05
Chlorine							222
Chromium							186.31
Cobalt							102.91
Copper							85.48
Curium							101.7
Dysprosium							150.43
Erbium							45.10
Europium							78.96
Fluorine							28.06
Francium							107.880
Gadolinium							22.997
Gallium							87.63
Germanium							32.066
Gold							180.88
Hafnium							(99)
Helium							127.61
Holmium							159.2
Hydrogen							204.39
Indium							232.12
Iodine							169.4
Iridium							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
Lutetium	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

* Values in parentheses are mass numbers for the most stable isotope.

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Ionic Equilibrium as Applied to Qualitative Analysis

IONIC EQUILIBRIUM AS APPLIED TO QUALITATIVE ANALYSIS

THIRD EDITION

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HOLT, RINEHART AND WINSTON
NEW YORK · CHICAGO · SAN FRANCISCO
TORONTO · LONDON

Copyright 1941, 1947, and 1954
by T. R. Hogness and Warren C. Johnson
Library of Congress Catalog Card Number: 54-6606

10-63

23686-0314

Printed in the United States of America

PREFACE

This text, *Ionic Equilibrium as Applied to Qualitative Analysis*, consists of the theoretical portion (Part I) and the Appendix of the revised edition of the complete text, *Qualitative Analysis and Chemical Equilibrium*. It is designed to meet the needs of teachers who either prefer to use their own particular scheme of analytical procedure or want to include in their courses supplementary material on chemical equilibrium in the form of problems and exercises.

In developing a course in qualitative analysis we have had several major objectives in view, one of which is the early introduction into the chemical curriculum of a thorough study of the important principle of chemical equilibrium. This principle is met in the explanation and understanding of almost every analytical separation and identification, and qualitative analysis therefore serves as an excellent medium for the study of this principle.

The presentation of this subject is based upon the assumption that the student is familiar with the atomic theory, the kinetic molecular hypothesis and its application to the behavior of gases, the meaning of atomic and molecular weights, the balancing of simple chemical equations, the most general properties of solutions, and, in an elementary way, the periodic system.

The revised edition represents a considerable expansion. We have added a chapter on the states of matter, one on the quantization of atoms and molecules, and a third on nuclear chemistry. It will be obvious to the instructor that some of this new material has little bearing on qualitative analysis *per se*. However, much of this new material is penetrating

chemical thinking so rapidly today that it cannot be neglected. Furthermore, we find that it is just this sort of material that the more ambitious students find fascinating. Should the instructor find that time is short, he can postpone Chapters 4 and 14 and a part of Chapter 11 without impairing the continuity of the subject matter. In these chapters an attempt is made to introduce the student to some of the newer concepts of the structure of molecules and to the principles governing the reactions of ions and molecules in the formation of complexes. It is felt that it is important at this point in the student's training to familiarize him with the ideas he will have to apply later in the chemistry curriculum.

The tables of equilibrium constants in the Appendix have been completely revised and greatly expanded to include more recent data. These tables of constants are now quite complete and include the latest information available in the literature. The most important change is in the ionization constants for hydrogen sulfide. Instead of using the old values which have been accepted for some fifty years we have adopted the recently published values of Latimer and colleagues (see Report UCRL–2108, University of California Radiation Laboratory, entitled "Heats of Formation and Entropies of HS^- and S^{--}. Potential of Sulfide-Sulfur Couple," February 12, 1953). This has necessitated an examination of the older literature and a re-evaluation of the solubility-product constants for the sulfides, since these values in almost all cases are calculated by making use of the hydrogen sulfide ionization constants. It was in this study that we became more appreciative of the unreliability of the solubility-product constants of the sulfides. In almost all cases it was found that the values of the constants vary greatly with time. Wherever possible, we use the best value obtainable for the freshly precipitated sulfide. Due to this variability with time we strongly recommend that precipitated sulfides not be allowed to stand for any protracted period before being dissolved. Negligence at this point can upset the analytical procedures.

The number of figures in the text has been increased con-

siderably, and so has the number of tables. Many sections of the text have been completely rewritten. The chapter on *Complex Ions* has been extensively revised with the view of providing the student with some of the modern ideas of quantized formation of molecular orbitals.

No attempt has been made to introduce the concept of activity or activity coefficients. This subject is not essential to a fundamental understanding of chemical equilibrium, nor is the student prepared to interpret its significance. In numerical calculations in this course its contribution is of no importance. We "violate" the Law of Mass Action in that we apply it to concentrations rather than to activities in the more concentrated solutions, and give answers to problems in figures which are often not significant. We justify this procedure on the grounds that such answers give the student a means of checking his thought processes involved in formulating the problems.

Descriptive material is interwoven with the presentation of the theoretical aspects of the subject, both of which are applied in numerous instances to qualitative analysis and general problems of chemistry. Each chapter concludes with a set of questions and problems. The questions serve as a guide for study and review of the subject matter. The several hundred problems deal essentially with equilibria of solutions. It is our conviction that the student cannot acquire an adequate understanding of chemical equilibrium and its application without dealing with numerical calculations involving this principle. It is not necessary that these calculations be mathematically difficult. Accordingly, special effort has been made to select relatively simple problems which are arranged in the order of increasing difficulty. Examples of all types of problems and their complete solutions are given at the end of each chapter. Answers to all problems and an ample section on mathematical operations are included in the Appendix as a guide for the student. New problems may easily be constructed from those given in the text.

We regard this presentation of the subject of equilibrium

in solutions complete enough to relieve the teacher of a considerable amount of time in its presentation again in a later course in physical chemistry.

T. R. H.
W. C. J.

March 15, 1954

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PART I

CHAPTER

1

The Atomic and Molecular Concept of Matter

Atoms, Molecules, and the States of Matter. Matter, which in its many forms makes up our universe, exists as a solid, a liquid, or a gas. But all matter consists of atoms and molecules. How then do the different states of matter — the solid state, the liquid state, and the gaseous state — differ from each other in terms of atoms and molecules?

In the solid crystalline state the molecules, and the atoms which make up the molecules, occupy definite fixed positions. There is a high degree of order, just as there is order among troops on review or parade. Although the positions of the molecules are fixed, the molecules are in a state of vibration. The higher the temperature the greater the vibration. At a sufficiently high temperature the molecules vibrate hard enough to overcome the forces holding them together, causing the crystalline solid to melt.

In the liquid state there is a great deal of randomness in the positions of the molecules but there is not complete confusion, for some of the molecules band themselves together in small but somewhat ordered groups. The higher the temperature of a liquid the greater the disorder, since, at higher temperatures, the molecules of a liquid move about faster or vibrate harder and thus knock the more ordered small groups apart.

The gaseous state is characterized by complete randomness

of molecular position — the molecules of a gas are constantly moving about and are not in any fixed or orderly position with respect to each other. The higher the temperature the greater is the velocity of these molecules.

As the temperature of a gas is lowered, the average collision gets less and less violent until the attractive forces between the slowest of the molecules come into play and these molecules then ban together to form droplets which settle out as a liquid. As the liquid is further cooled, order begins to take place and finally the liquid solidifies, usually in the form of crystals but sometimes as a glass. When the solid is cooled the vibrations of the molecules in the solid get less and less violent until these vibrations no longer exist or are reduced to the lowest possible vibration state. At this point, the temperature has reached absolute zero, below which it cannot go — below which temperature has no meaning.

The Nature of Crystalline Solids. If we examine grains of ordinary table salt under a magnifying glass, we see that all of these grains appear to be cubes. Furthermore, if we should measure the angles between the faces of these cubes with a goniometer (a special microscope used by mineralogists to measure the angles between crystal faces), we would find these angles to be exactly 90° — not 89° 59′ or 90° 1′ but exactly 90°. Likewise, if we were to measure the angle between the predominating faces of a quartz crystal, we would find it to be exactly 120°. All crystals have very definite and, in many cases, simple angles between the crystal faces.

The fact that crystals assume very definite shapes indicates strongly that the atoms and molecules of which they are composed are arranged in very definite and ordered positions. The order in which atoms are arranged and the distances between the various atoms have been determined by X-ray diffraction and, to a lesser extent, by electron diffraction measurements. We shall omit the details of these methods in this course and accept the results as conclusive.

X-ray diffraction analysis shows that in sodium chloride each chlorine particle is surrounded by six sodium particles

and each sodium particle is surrounded by six chlorine particles. Furthermore, such an analysis shows that the axial distance between the centers of the sodium and chlorine particles is 2.81 Å. (Å is the abbreviation for Ångstrom unit which is equal to 1/100,000,000 or 10^{-8} cm.) Actually the sodium and chlorine particles in this crystal are in the form of ions. The sodium ion is positively charged and the chlorine ion is negatively charged. This differentiation will be considered

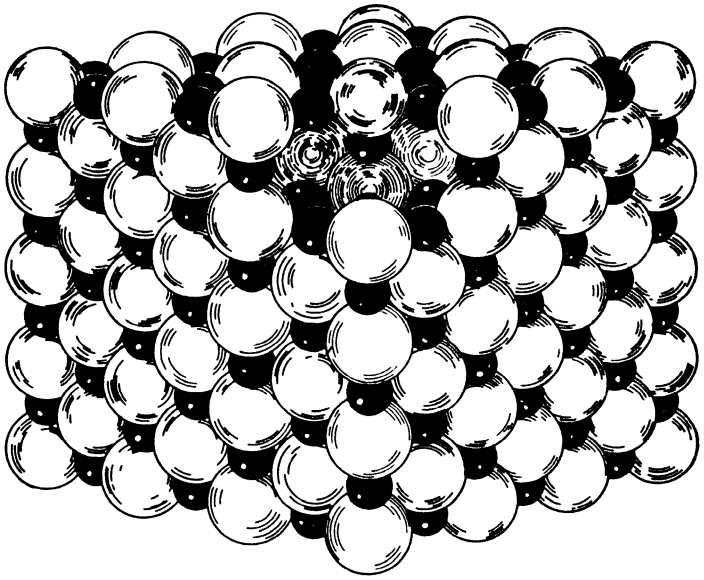


FIG. 1.1 The crystalline form of sodium chloride.

more fully in the following chapters. The arrangement of the sodium and chlorine particles with respect to each other in the sodium chloride crystal is shown in Figure 1.1.

Note that the chlorine particles have about twice the diameter of the sodium particles. From this figure it is easy to see that each particle is surrounded by six immediate neighbors of the other kind. Crystallographers describe this situation by saying that the *crystal coordination number* of the sodium and of the chlorine is six in sodium chloride.

It is apparent that with such an arrangement of Na and Cl

particles the angles between the faces should be exactly 90°. NaCl crystals tend to grow in such a way as to produce cubes or rectangular hexahedra. But the cubic arrangement of the particles in NaCl does not mean that such an arrangement of particles will always yield crystals of this type. For example, the structure of a crystal of KCl is exactly like that of NaCl yet KCl crystals are most often found in the form illustrated in Figure 1.2.

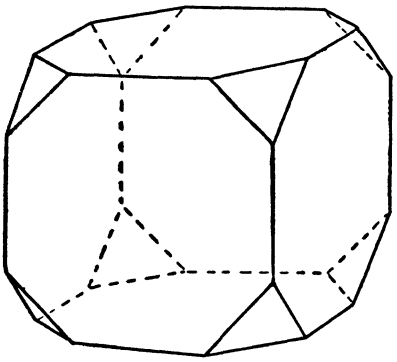


FIG. 1.2 The crystalline form of potassium chloride.

In general, crystals tend to grow in such a way as to produce the maximum concentration of atoms on the surface. While the arrangement of the particles in NaCl and KCl is the same, there is a difference in that the potassium particles (or ions) are considerably larger than the sodium ions. This difference in relative size changes the packing in the various planes and to some extent changes the macroscopic appearance of the crystal. A cubic arrangement of particles can therefore manifest itself in several crystalline forms.

When all the atoms are alike, as in the case of metals, the atoms tend to pack together as closely as possible. The simplest close packing is hexagonal. In beryllium and magnesium, for example, the atoms are arranged in layers as illustrated in Figure 1.3.

The second layer of atoms does not fit directly over the first, but each atom in the second layer lies in the depression between three adjacent atoms of the lower layer — the points marked *X* in Figure 1.3. The third layer lies immediately over layer 1. The arrangement of layers is therefore A–B–A–B–A–B, etc. Each atom has 12 equidistant neighbors.

The structures of copper, silver, and gold are examples of cubic close packing. In these cases each layer of atoms is the same as that for the hexagonal close-packing structure. In cubic

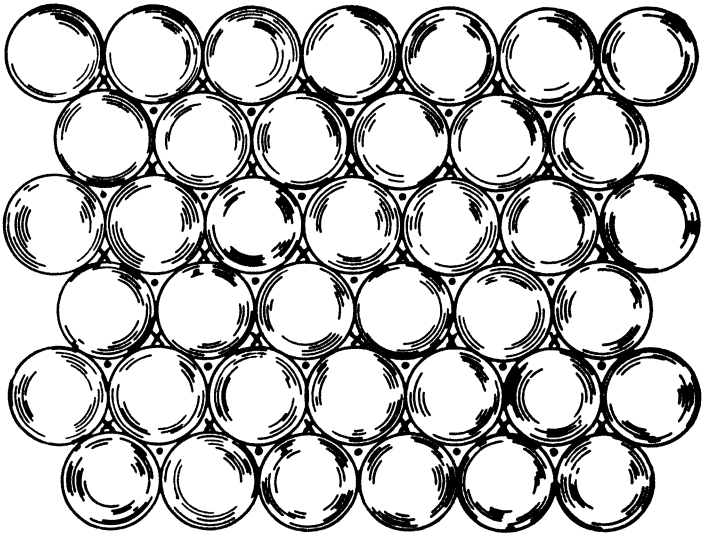


FIG. 1.3 Hexagonal close packing of atoms.

close packing the atoms of the second layer (see Figure 1.3) fall into the positions marked *X* as in hexagonal close packing, but the atoms of the third layer, instead of lying directly over those in the first layer, lie over the positions marked with a dot in the first layer. The atoms of the fourth layer then lie over those in the first. The arrangement of layers is A–B–C–A–B–C–A–B–C, etc. Along certain axes the atoms have a cubic arrangement. Each atom in this structure is also surrounded by 12 equidistant neighbors. The crystal coordination number is 12.

The other close-packing structure common to metals is body-centered close packing which is really not "close packing." In this case the atoms of each layer are arranged in rows at right angles to each other. Each atom of the next layer lies in the depression between four atoms of layer 1. The atoms of the third layer lie above those in the first. Examples of this structure are molybdenum, tungsten, and the alkali metals.

Most metals have one of the above three structures; a very few have combinations of two of these.

The Liquid State. We know much less about the condition of molecules in the liquid state than we do for that in either the gaseous or solid states. The molecules of a liquid adhere to each other and the fluidity of liquids indicates that the molecules have the ability to move about or slip over each other. As we have previously indicated, X-ray evidence supports the view that very probably the molecules in a liquid tend to line up with each other to some extent and that this aligning tendency is greater the lower the temperature. In most liquids, however, some of the molecules are probably already arranged in the form of the solid crystal. These nuclei act as the growth centers for crystal formation when the temperature is sufficiently low.

When ordinary glycerine is cooled, it solidifies to form crystalline glycerine at 17° C. On the other hand, if it is kept at a temperature far above its melting point for a protracted time and then is cooled below the melting point, the glycerine gradually becomes more and more viscous until a glass is formed. If the glass is now melted and subsequently cooled, a glass is formed again, unless the liquid is seeded by the addition of glycerine crystals or of glycerine which itself will crystallize on cooling. Evidently, ordinary glycerine contains some nuclei or incipient crystals which act as the starting point for crystallization but which are destroyed at high temperatures. Liquids differ markedly in their ability to form glasses or supercooled liquids (i.e., cooled below the freezing point).

When quartz (silicon dioxide) crystals are melted (the melting point of quartz is about 1400° C), the temperature is so high that there are practically no crystal nuclei left in the melt. If the quartz is then cooled so rapidly that nuclei do not have much chance of forming, the liquid gets more and more viscous and finally becomes a solid glass. In this condition the silicon dioxide molecules have attached themselves to each other to form an irregular pattern which contains some atomic-sized holes or voids. This condition is illustrated in Figure 1.4.

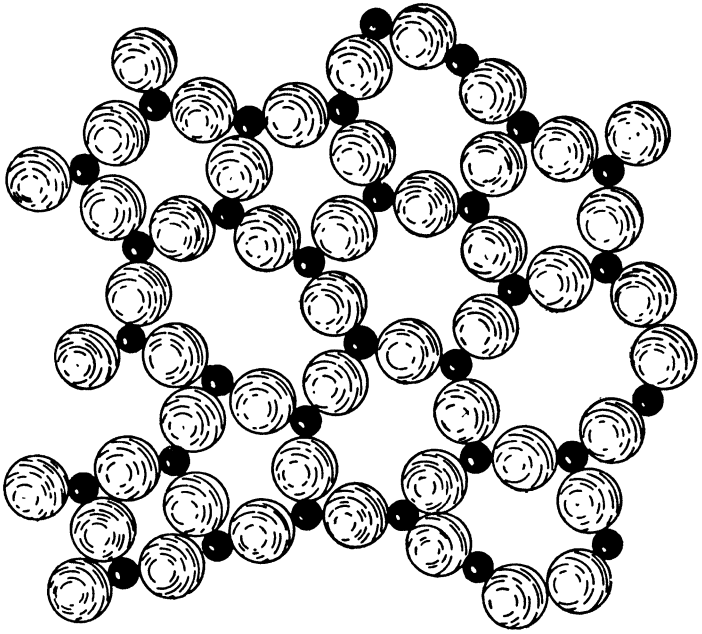


FIG. 1.4 Schematic representation of quartz glass. The black spheres represent silicon, and the lighter spheres, oxygen particles. (According to Zachariasen.)

It is to be noted that Figure 1.4 is only a two-dimensional representation. Each silicon atom has four oxygen atoms surrounding it. The silicon atoms in Figure 1.4 therefore have oxygen atoms attached to them either above or below the plane shown in the figure.

When a liquid containing no nuclei is cooled it will not form crystals and will therefore become what is known as a *supercooled liquid*. If a beaker of water is cooled to 0° C it will form ice because either the water itself contains a few ice nuclei or, more likely, because the glass surface acts as nuclei to bring about the initial crystalline ice formation.

When a very small droplet of water is suspended in air, as in a cloud, it can often be cooled to as low a temperature as −40° C with no formation of ice. Such small droplets of water contain no ice nuclei. The temperatures of the tops of many cumulus clouds (thunderheads) are well below the freezing

point of water. When the temperature gets very low (below −40°) the motion of the molecules becomes so sluggish that nuclei form and the particle turns to ice. These minute ice crystals then grow and as they fall through the warmer part of the cloud they melt and grow larger by accumulating other small droplets. When they strike each other they break up into smaller drops. These drops are lifted by the turbulent wind in the cloud and grow larger. This process repeats itself and rain falls out of the cloud. This is one of the mechanisms of rain formation.

Rain can be produced artificially by seeding the upper part of a cloud with artificial nuclei. One of the best seeding agents is silver iodide. This substance has a crystal structure much like ice, and water molecules use these tiny crystals of silver iodide as nuclei on which to grow ice crystals. Solid carbon dioxide (dry ice) at −80° C is also used for seeding. In this case the low temperature allows a small fraction of the cloud droplets to nucleate themselves.

This phenomenon of crystal nuclei in liquids is of great importance in the science of metallurgy. When many nuclei are present, a fine grain structure is formed on solidification. When few nuclei are present, the grain structure is coarse. In most cases large grain size in metals is undesirable. Molybdenum often shows this phenomenon to a high degree. When a large melt of molybdenum is cooled it often solidifies in extremely large grains, sometimes a foot in length. This phenomenon is not always easy to control. The study of crystal nuclei, particularly in metals, is still in its infancy.

Polarity of Molecules. Suppose that two large sheets of metal are connected electrically with a battery B, a switch and a current-measuring instrument as shown in Figure 1.5. When the switch S is closed, the plate connected to the negative pole of the battery becomes negatively charged and the plate connected to the positive pole of the battery positively charged. Just at the moment the switch is closed the small current charging the plates will flow through and be measured by the current-measuring instrument. The positive charges

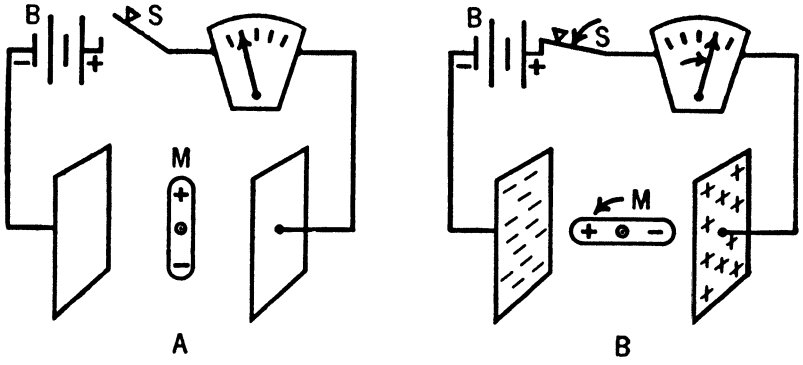


FIG. 1.5 Action of electric field on polar molecule.

on the one plate attract the negative charges of the other and vice versa, and this attraction builds up the charge-holding ability or capacity of the two plates. If the size of the plates is increased, it is obvious that the two plates will hold a greater electric charge, that is, the capacity will be increased.

The nearer two oppositely charged objects are to each other the greater is the attractive force between them. If the two plates are moved closer together the attractive force which holds the charge on the surface of each plate becomes greater and the two plates therefore have a greater capacity. One might argue that as the charge increases on each of the plates the attractive force will also increase, resulting in an accumulatively greater capacity. There is an opposing force, however, which stops this accumulative effect. Like charges *on the same plate* repel each other and this repulsive force, which is greater as the charge on each plate is increased, prevents any indefinite accumulation of charge on any one plate. Such an arrangement of plates is known as a condenser.

Suppose that a bar *M* which can pivot about its center and which has one end positively charged and one end negatively charged is placed between the two plates. When the plates are now charged the bar will be found to tilt in such a position that the positive end will move toward the negative plate (Figure 1.5B). Such a bar will increase the electrical capacity of the two plates, for this action of the bar will have the effect

of putting the two plates closer together. The positive end of the bar will produce an attractive effect on the negative plate; and the negative end, an attractive effect on the positive plate.

Many molecules are like the bar shown in Figure 1.5. They have positive and negative ends and when placed between two such charged plates tend to line up as does the bar. This alignment increases the electrical capacity of the plates as measured by the current-measuring instrument.

The ratio of the electrical capacity of the condenser when some substance is placed between its plates to the electrical capacity when there is a vacuum between these same plates is known as the ***dielectric constant*** of the substance.

$$\frac{\text{capacity with substance}}{\text{capacity in vacuum}} = \text{dielectric constant}$$

The greater the separation of the positive and negative charges in a molecule, the greater will be the turning effect on the molecule in the condenser, and therefore the greater will be the capacity of the condenser and the greater the dielectric constant of the substance. In Figure 1.6, the molecule *B* has a greater turning effect than molecule *A*. Since a greater separation of charge produces a greater torque or electrical leverage, molecule *B* can be more easily turned than molecule *A*. Therefore *B* has a greater dielectric constant than *A*. The dielectric constant is then a measure of the separation of the charges in a molecule.

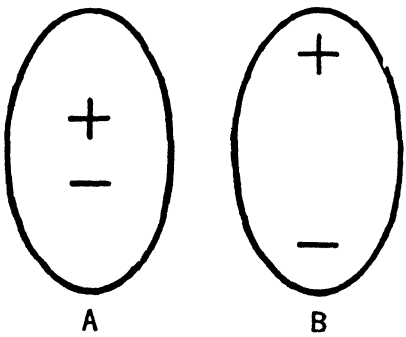


FIG. 1.6 Schematic representation of two polar molecules. *B* more polar than *A*.

Not all the molecules placed between the plates of a condenser are turned at right angles to the plates as shown in the case of the charged bar (Figure 1.5). The thermal agitation

of the molecules prevents perfect alignment. We can deduce that the lower the temperature the less will be the thermal agitation and the greater will be the alignment. The dielectric constant of a polar molecule should therefore decrease with increasing temperature. This conclusion is completely verified by experiment.

Polar and Non-Polar Substances. Those substances which have a large dielectric constant, that is, a large separation in the charges, are known as polar substances and those which have little or no separation in charges as non-polar substances. Water is a polar substance and methane, CH_4, and hexane, C_6H_{14}, a constituent of gasoline, are non-polar substances. We shall have more to say regarding such substances at a later time.

Vapor Pressure and the Boiling Point. Suppose that a pure liquid is confined in a closed vessel and all extraneous gases such as air are removed from the space above the liquid. (See Figure 1.7). Then it is found that at a given, definite temperature there will be a definite gas pressure due to the evaporated molecules of the liquid. An equilibrium is established between the liquid and the gas, such that the rate of gas molecules entering the liquid is the same as that of molecules of liquid leaving it to enter the gas phase. This pressure can be measured by some suitable device such as a manometer shown in Figure 1.7, and it is known as the vapor pressure of the liquid for that temperature. Thus, the vapor pressure of water at 25° C is 25.76 mm. of mercury.

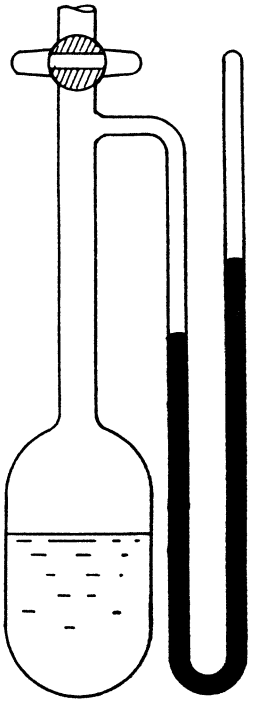


FIG. 1.7. Schematic diagram of apparatus for determining vapor pressure.

When a liquid is heated in an open vessel such as a beaker, vapor is constantly passing off into the air above it. However,

when the temperature of the liquid gets sufficiently high so that its vapor pressure equals the pressure of the air above it, the liquid boils. This boiling temperature evidently will depend upon the barometric pressure. The *normal boiling point* of the liquid is defined as the temperature at which the liquid boils when the barometric pressure is 760 mm. of mercury. In other words, the *normal boiling point* is the temperature at which the vapor pressure of the liquid is 760 mm. of mercury.

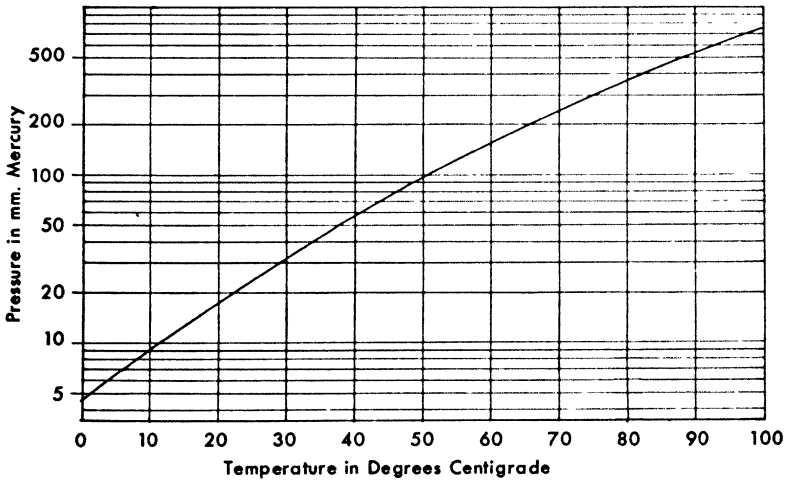


FIG. 1.8 The vapor pressure of water as a function of the temperature.

By plotting the vapor pressure of a liquid against the temperature one obtains a curve such as is illustrated in Figure 1.8.

We might expect that the boiling points of non-polar liquids, for which the attractive forces between the molecules are very similar, would depend upon the molecular weight of the compound in such a way that the greater the molecular weight, the higher the boiling point. The heavier molecules move more slowly at any given temperature; therefore, a higher temperature is required for them to escape from the liquid. If we compare the non-polar hydrocarbons as shown in Table 1, we find this to be the case.

If the forces holding water molecules together were the same as those for the hydrocarbons shown in Table 1, then,

TABLE 1

RELATIONSHIP BETWEEN MOLECULAR WEIGHT AND BOILING POINT

Compound	Molecular Weight	Boiling Point, ° C
Methane, CH_4	16	−161.8
Ethane, C_2H_6	30	−88.6
Propane, C_3H_8	44	−42.1
Butane, C_4H_{10}	58	−0.5
Pentane, C_5H_{12}	72	36.1
Hexane, C_6H_{14}	86	68.7

since its molecular weight approximates that of methane, we might expect its boiling point to be essentially the same. However, the boiling point of water is 100° C; 261.5° higher than that of methane. Ammonia (NH_3) has a molecular weight of 17. It is also a polar liquid but not as polar as water. Its boiling point is −33.4° C. These facts show the great effects which can be produced by unequal distribution of electric charges within the molecule. Similar effects due to polarity will be encountered when we study the problem of solubility.

The Problem of Solubility. Some substances are soluble in each other in all proportions, while some are only so slightly soluble that we say they are insoluble. This difference in solubility of various substances in the same or different solvents has been a subject of the greatest concern for the chemist. It is a problem which is so complex that its quantitative solution offers great difficulties, yet the fundamental principles involved are not at all out of our reach.

Let us consider two liquids which are practically insoluble in each other. There are a great many systems of pairs of liquids which conform to this condition of low mutual solubility, but as a specific example we shall choose water and carbon tetrachloride. The water molecules are polar and those of carbon tetrachloride are non-polar. By virtue of their

polarity, the water molecules have a greater tendency to adhere to each other (the positive end of one adhering to the negative end of another) than to molecules of carbon tetrachloride. As a result of the attractive forces of the water molecules for each other, any molecules of carbon tetrachloride which happen to be mixed with the water molecules are squeezed out. Due to thermal agitation, a few water molecules will probably break through the water surface in contact with carbon tetrachloride and wander off into this medium. For this reason, we cannot say that water and carbon tetrachloride are absolutely immiscible (absolutely insoluble in each other). The water molecules prefer each other to the molecules of carbon tetrachloride as neighbors. Likewise the molecules of carbon tetrachloride prefer each other. The polar dissimilarity of these two types of molecules, in a general way, accounts for the insolubility of water and carbon tetrachloride in each other.

Let us next consider a solution of two substances the molecules of both of which are polar. Water and ordinary alcohol are two such substances. The water molecules are somewhat more polar than the alcohol molecules. In this case the water molecules do not have any very great tendency to prefer each other as neighbors and the same is true of the alcohol molecules. The water molecules adhere to the alcohol molecules almost as strongly as they do to each other. Now there is no tendency for the water molecules to squeeze the alcohol molecules out of solution, nor do the alcohol molecules have this tendency toward water molecules. The result is that water and alcohol are soluble in each other in all proportions.

Non-polar substances are also soluble in each other, for there is no great tendency for the like molecules to prefer each other as neighbors; hence no "squeezing-out" effect.

No new considerations need be introduced in the problem of the solubility of solids in liquids. The attractive forces of the particles for each other in the crystal, in general, are very great; nevertheless there will be competition between the crystal and the solvent for the particles of the solid. The stronger the

crystal forces operating between the atoms or particles of the solid and the greater the "squeezing-out" tendency of the solvent, the less soluble will be the solid in question.

It is possible to arrange substances in a series or table in order of the attractive forces operating between the molecules. An example of such a series is given in the following table. The non-polar substances appear at the top of the table and the polar substances at the bottom. Two substances lying close together in the series are very soluble in each other; those far apart are relatively insoluble in each other.

TABLE 2

RELATIVE ATTRACTIVE FORCES BETWEEN MOLECULES

Hexane	
Carbon tetrachloride	
Benzene	
Toluene	NON-POLAR ↑
Chloroform	
Naphthalene	
Anthracene	
Nitrobenzene	
Pyridine	
Carbon bisulfide	
Acetone	
Acetic acid	
Ethyl alcohol	
Methyl alcohol	
Water	POLAR ↓

Some organic molecules are so complicated in structure that parts of the molecule may be regarded as polar and other parts as non-polar. With such substances the problem of solubility is necessarily a much more complex one.

The compound, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$, octyl alcohol, for example, consists of a long chain of carbon atoms, to one end of which is attached an OH radical. This OH end of the molecule is polar and the other end is non-polar. When

placed in contact with water, only one end of the molecule is squeezed out of solution and the other end remains in contact with the water. The result is that the octyl alcohol molecule is squeezed to the surface of the water, with one end out of solution. Such phenomena are common and are of great interest in the study of surface chemistry.

There is one type of solution, electrolytic solution, which we have not yet considered and to which we shall later largely confine our attention. Before going on with the problems of solubility pertaining to such solutions, we must first deal with some of their properties.

Molecular Weights and Formula Weights. From a knowledge of the composition of a pure compound and from the atomic weights of its constituent elements it is possible to determine the simplest formula, but only the simplest formula, of the substance. For example, sodium chloride is found by analysis to contain 39.34 percent sodium. From this information and from the atomic weights of sodium and chlorine it can be determined that in sodium chloride there is one atom of chlorine for every atom of sodium.* The simplest formula for sodium chloride is therefore NaCl. This does not tell us that the molecule of sodium chloride consists of only one atom of chlorine and one of sodium; e.g., it might contain two or more atoms of each. In fact, there is no simple molecule of sodium chloride in the solid state for, as we have previously shown, each atom of sodium is surrounded by six chlorine and each chlorine by six sodium atoms. No chlorine atom is associated with any particular sodium atom. For solid sodium chloride then, the term molecular weight has no definite meaning, if we wish to be very exact in our concepts and definitions, since the molecular weight is the relative weight of the *molecule* as compared with the weight of a *molecule* of oxygen gas. For such a case we may use the term ***formula weight*** instead of molecular weight.

The terms molecular weight and formula weight are often used interchangeably, but we must guard against loose think-

* For this calculation see some text in general chemistry.

ing in doing so, since it might easily be implied that the molecule of solid sodium chloride consists of one atom of sodium and one atom of chlorine, which is not the case.

Iodine in the gaseous state is diatomic and its formula is I_2. It has been shown that in the solid state its formula is also I_2, for in solid iodine two iodine atoms remain attached as a molecule, that is, each iodine atom has associated with it one other atom more tightly bound than the rest. Many substances including all organic compounds behave like iodine, but most inorganic substances are like sodium chloride in that the molecule of the solid is not a definite entity.

The Concentration of a Solution. The simplest kind of a solution is made up of two components, the ***solvent*** and the ***solute.*** In general, the component present in the larger amount is known as the solvent, the other component, the solute. Thus, for a solution consisting of a large amount of water and a small amount of alcohol, water is the solvent and alcohol, the solute. If the alcohol were present in the larger amount, it would be the solvent and the water would be designated as the solute. However, for solutions consisting of water and an inorganic substance we shall arbitrarily refer to water as the solvent in all cases. A solution of sulfuric acid may be so concentrated that water is present in the smaller amount; nevertheless, we shall still regard the water as the solvent. In this course we shall be concerned chiefly with only three types of solutions, namely, gases, liquids and solids dissolved in water.

The amount of the solute dissolved in a given quantity of water determines the ***concentration*** of the solution. The quantitative expression for the concentration may be defined in a number of ways.

Weight-percent Solutions. The concentration of a weight-percent solution is expressed in terms of the number of parts of solute by weight contained in 100 parts of the solution. Thus 100 grams of a 36-percent solution of hydrochloric acid by weight contains 36 grams of HCl and 64 grams of water.

Molal Solutions. The ***molal*** concentration of a solution is

defined as the number of gram-molecular-weights or gram-formula-weights of solute dissolved in 1000 grams of water. In qualitative analysis we shall have no need to use solutions the concentrations of which are defined in this way.

Molar Solutions. The ***molar*** concentration of a solution is defined as the number of gram-molecular-weights (***moles***) or gram-formula-weights dissolved in 1 liter of *solution*, i.e., in enough water to produce 1 liter of solution. Thus, a 2 molar solution of NaCl may be prepared by adding enough water to 116.92 (2×58.46) grams of NaCl so that the final volume is exactly 1 liter. The ***molarity*** (moles per liter) of this solution is 2 moles NaCl per liter or 2 *M* NaCl. A 2 *M* NaCl solution could also be prepared by adding enough water to 11.692 grams of NaCl to make 100 ml. (0.1 liter) of solution.

The concentration of a solution bears no relation to the amount of solution. If the concentration of a solution is designated as 2 *M* then every drop, every milliliter, every liter or even every barrel of that solution has the same concentration, 2 *M*.

The number of moles of a solute contained in a given amount of solution is never equal to the molarity of that solution unless the volume should happen to be exactly 1 liter. The number of moles of a solute contained in any solution is equal to the molarity multiplied by the volume of the solution expressed in liters. In 1 ml. of a 2 *M* NaCl solution there is present $.001 \times 2$ moles or .002 moles of NaCl. It is to be observed that a 2 *M* solution may also be defined as one which contains 2 *millimoles* per *milliliter* (a millimole is .001 mole and a milliliter is .001 liter).

$$\frac{.002 \text{ mole}}{.001 \text{ liter}} = \frac{2 \text{ moles}}{1 \text{ liter}} = 2\ M$$

In this text the concentrations of solutions will always be expressed in terms of molarity.

Normal Solutions. The concentration of a solution is said to be 1 normal (1 *N*) when enough water is added to 1 gram-equivalent-weight of the solute to make 1 liter of the solution.

Concentrations expressed in terms of normality are very convenient in quantitative volumetric analysis, but use of normal rather than molar solutions offers no decided advantage in this course. We shall therefore not be concerned with this method for expressing concentration.

Examples of Problems

Example 1.

How many grams of KBr will be needed to make 150 ml. of a 2 *M* solution?

1 mole (formula weight) KBr = 39.1 + 79.9 = 119.0 g.

2 moles KBr = 2 × 119.0 = 238 0 g.

1 liter of a 2 *M* KBr solution contains 238.0 g.

1 ml. of a 2 *M* KBr solution contains 0.238 g.

150 ml. contains 150 × 0.238 = 35.7 g.

Therefore, if enough water is added to 35.7 g. KBr to make 150 ml. a 2 *M* solution will be obtained.

Example 2.

It is desired to make a 0.1 *M* solution by adding water to 5 g. of $AgNO_3$. What must be the final volume of the solution after all the water is added?

1 mole $AgNO_3$ = 107.9 + 14.0 + 3 × 16 = 169.9 g.

A 0.1 *M* $AgNO_3$ solution contains 16.99 g. per liter or .01699 g. per ml.

5 g. $AgNO_3$ furnishes enough for $\frac{5}{.01699}$ or 294 ml.

Example 3.

How many ml. of water must be added to 5 ml. of 12 *M* HCl solution to make a 3 *M* HCl solution?

NOTE: *In all dilution problems we shall assume that the final volume is equal to the volume of the initial solution plus the volume of the water added; i.e., that the volume occupied by all molecules or ions is the same in solutions of all concentrations.*

In 1 ml. of a 3 *M* solution there are $\frac{3}{12}$ or $\frac{1}{4}$ as many molecules as there are in 1 ml. of a 12 *M* solution. Therefore, enough water must be added to the 12 *M* solution to make its final volume 4 times as great as it was originally. In this problem the final volume must be

4×5 ml. or 20 ml. Therefore 15 ml. of water must be added. In brief, the final volume must be 5×12 ml.

The amount of water added is $5 \times \frac{12 - 3}{3} = 15$ ml. In general, the volume of water added equals the *initial volume of solution* multiplied by $\frac{C_2 - C_1}{C_1}$ where C_2 is the larger concentration and C_1 the smaller.

Example 4.

How many ml. of a 2 *M* HCl solution is necessary to neutralize 3 ml. of a 0.5 *M* NaOH solution?

1 mole HCl neutralizes 1 mole NaOH.

The same number of moles of HCl are required as there are moles of NaOH in 3 ml. of a 0.5 *M* NaOH solution.

If the HCl solution were 0.5 *M*, instead of 2 *M*, equal volumes of each would be required. But the HCl is 2 *M* or 4 times as concentrated as the NaOH therefore less is required. Specifically, $\frac{1}{4}$ as much would be required as would be the case if the HCl were 0.5 *M*.

Number of ml. of HCl required $= 3 \times \frac{0.5}{2} = 0.75$ ml.

Example 5.

How many ml. of 6 *M* H_2SO_4 would be required to neutralize 100 ml. of 3 *M* NaOH?

Since the H_2SO_4 contains 2 replaceable H atoms (H^+ ions) and NaOH contains only 1 replaceable OH radical (OH^- ion), one-half as many moles H_2SO_4 are required as the number of moles of NaOH contained in 100 ml. of 3 *M* NaOH.

If the H_2SO_4 were 1.5 *M*, instead of 6 *M*, 100 ml. would be required, but with 6 *M* H_2SO_4 the amount required would be $100 \times \frac{1.5}{6} = 25$ ml.

Example 6.

What is the molarity of a H_2SO_4 solution which contains 33.33 percent H_2SO_4 by weight and which has a density of 1.25?

One liter of the solution weighs 1000×1.25 or 1250 g.

The number of grams of H_2SO_4 in one liter is 0.3333×1250 or 417 g.

One mole of H_2SO_4 is 98.1 g. The number of moles in one liter is $\frac{417}{98.1} = 4.25$ moles per liter. The solution is therefore 4.25 *M*.

Questions and Problems

1. What is the distinction between a glass and a crystalline solid?
2. Account for the fact that glycerine, when cooled to a sufficiently low temperature, in some cases solidifies to form a glass, and in other cases, to form a crystalline solid.
3. What is the dielectric constant of any given substance?
4. How does a polar molecule differ from a non-polar one?
5. Taking into account the thermal agitation of molecules, explain why the dielectric constant for a given substance is lower the higher the temperature of the substance.
6. Does a molecule of solid sodium chloride consist of one ion of sodium and one of chlorine? Explain.
7. Explain why two liquids, one of which consists of polar molecules and one of non-polar molecules, are immiscible in each other.
8. What is the molarity of a solution which contains 5 g. HCl in 100 ml. of solution?
9. How many moles of NaOH are contained in 200 ml. of a 0.5 *M* solution?
10. How many grams of H_2SO_4 are there in 40 ml. of a 0.1 *M* H_2SO_4 solution? (H=1, S=32, O=16)
11. If 27 ml. of water is added to 35 ml. of a 0.1 *M* solution of any substance, what is the molarity of the final solution?
12. (a) How many moles are 5.85 g. of NaCl? (Use 23.0 as the atomic weight of sodium and 35.5 as the atomic weight of chlorine.)
    (b) If this amount of NaCl is dissolved to make one liter of solution, what is the molarity of the solution?
    (c) If this amount of NaCl is dissolved to make 500 ml. of solution, what is its molarity?
13. How many grams of solute are contained in each of the following solutions?
    (a) 250 ml. of 0.1 *M* $MnCl_2$ solution
    (b) 500 ml. of 5 *M* H_2SO_4 solution
    (c) 25 ml. of 2 *M* Na_2CO_3 solution
    (d) 12 ml. of 0.1 *M* $AgNO_3$ solution
    (e) 125 ml. of 0.5 *M* $BaCl_2$ solution

    (Assume the solute to have the formula indicated in each problem, i.e., unhydrated. See inside front cover for atomic weights — use only first figure beyond decimal point.)

14. If, in each of the following cases, it is desired to make a 0.1 *M* solution, what must be the final volume of the solution after the addition of water?
(a) 10 g. NaCl, (b) 20 g. $AgNO_3$, (c) 10 g. $HgCl_2$, (d) 10 g. $Na_2SO_4 \cdot 10H_2O$, (e) 1 g. $CuSO_4 \cdot 5H_2O$

15. How many ml. of water must be added to each of the following solutions to give the desired concentration?
(a) 10 ml. 6 *M* HCl to give a 2 *M* solution
(b) 25 ml. 2 *M* H_2SO_4 to give a 0.1 *M* solution
(c) 6 ml. 0.1 *M* $AgNO_3$ to give a .01 *M* solution
(d) 35 ml. 1.5 *M* H_2SO_4 to give a 0.3 *M* solution
(e) 2 ml. 0.3 *M* NaCl to give a 0.25 *M* solution

16. How many ml. of 0.1 *M* $AgNO_3$ solution and how many ml. of water must be mixed to give 250 ml. of .03 *M* $AgNO_3$ solution?

17. How many ml. of 0.1 *M* HCl solution is required to neutralize 25 ml. of 0.3 *M* NaOH solution?

18. How many ml. of 0.1 *M* H_2SO_4 solution is required to neutralize 25 ml. of a 0.3 *M* KOH solution?

19. How many ml. of a 1.5 *M* HCl solution is required to neutralize 75 ml. of a 0.2 *M* NaOH solution?

20. How many ml. of a 0.1 *M* HNO_3 solution is necessary to neutralize 15 drops of a 1 *M* NaOH solution? (Assume that 20 drops equals 1 ml.)

21. What is the molarity of each of the following solutions?
(a) 93.1 percent H_2SO_4 by weight (Density is 1.835)
(b) 32.3 percent HNO_3 by weight (Density is 1.200)
(c) 40.0 percent HCl by weight (Density is 1.200)
(d) 16.0 percent NaOH by weight (Density is 1.180)

The following review problems cover material not treated in this text. If necessary the student should refer to any general chemistry text for help.

22. A flask is filled with NH_3 gas at 76 cm. pressure and at 25° C. After a catalyst has been placed in the flask it is sealed. The flask is then heated and the NH_3 is completely converted into H_2 and N_2 in accordance with the equation

$$2NH_3 = 3H_2 + N_2$$

What is the total pressure of the mixed gases after the flask has again been cooled to 25° C?

23. What percent of lead is there in each of the following oxides: (a) PbO, (b) PbO_2, (c) Pb_2O_3, and (d) Pb_3O_4?

24. Ten grams of $CuSO_4 \cdot 5H_2O$ is heated to drive off the water of crystallization. After dehydration what is the weight of the anhydrous $CuSO_4$?

25. One hundred grams of iron combine with 30.1 liters of oxygen, measured at standard conditions, to form a solid oxide. What is the formula of the oxide?

26. Lead oxide decomposes to form oxygen in accordance with the following equation

$$2PbO_2 = 2PbO + O_2$$

How many grams of PbO_2 are necessary to give 22.4 liters of O_2, measured at standard conditions?

27. How many grams of oxygen will combine with 10 g. of magnesium to form MgO?

28. Assuming that a certain iron ore were pure Fe_2O_3 calculate the maximum number of pounds of iron that could be obtained from one ton of this ore.

29. 1.000 g. of copper is placed in a crucible covered with sulfur and heated out of contact with air. A reaction takes place between the copper and the sulfur. After the reaction is complete the excess sulfur is burned off as SO_2. The residue in the crucible now weighs 1.253 g. How many atoms of copper combine with one atom of sulfur? What is the formula for the sulfide of copper?

30. An oxide of chromium contains 68.4 percent chromium and 31.6 percent oxygen. What is its formula?

31. The chloride of a certain metal contains 64.1 percent of chlorine. What is the equivalent weight of the metal?

32. A 68.0 weight percent solution of sulfuric acid has a specific gravity of 1.587. What is the molarity of this solution?

33. What volume of the solution in question 32 would be necessary to make 1 liter of a 0.1 *M* solution?

34. What volume of 0.1 *M* HCl would be necessary to precipitate all the silver from a solution containing 1.00 g. of $AgNO_3$? (Assume that all the silver in solution will be precipitated as AgCl.)

35. Beginning with 0.1 *M* solutions of $AgNO_3$, $Pb(NO_3)_2$ and $Hg_2(NO_3)_2$, how many ml. of each must be added to enough

water to make 1 liter of a solution which is .02 M with respect to each of the ions, Ag^+, Pb^{++}, and Hg_2^{++}?

36. (Optional) The lift of any given airplane is proportional to $\frac{\rho V^2}{M}$ where ρ is the density of the air, V is the velocity of the airplane, and M is the total weight of the plane. Suppose that a given airplane must go 200 miles per hour to lift 100,000 pounds when the temperature of the air is 0° C and the barometric pressure is 760 mm. Suppose now that this same plane takes off when the barometric pressure is 750 mm. and the temperature is 38° C (100° F).

(a) Assume the load M to the same, using Boyle's and Gay-Lussac's laws, calculate what the take-off speed will have to be.

(b) Assume the take-off speed to be the same, i.e., 200 miles per hour (the maximum the airfield will permit), with what load can the airplane now take off?

37. (Optional) Can an airplane take off with a greater or smaller maximum load on a humid day as compared with a dry day, the temperature and barometric pressure being the same on the two days?

CHAPTER

2

Electrolytes and Non-Electrolytes

In this chapter we shall deal primarily with the properties of solutions of substances in water. From these properties we shall arrive at a distinction between electrolytes and non-electrolytes, thus giving the basis for our using ionic equations throughout the course.

Conductance of Electricity by Solutions. We shall compare the conductance of electricity by solutions of different substances. Such a comparison will allow us to divide practically all substances into two general classes, ***electrolytes*** and ***non-electrolytes.*** The conductance of any substance is the inverse of the resistance offered by the substance to the passage of the electric current, that is, $C = 1\ R$, where C and R represent the conductance and resistance, respectively. Conductance, like resistance, is determined by measuring the electric current passing through the substance when a definite voltage is applied between the two terminals of the containing cell. For a given voltage the amount of current is proportional to the conductance, that is, a solution having twice the conductance of another will allow twice as much current to pass through it for the same applied voltage.

In order to compare the conductances of solutions it is necessary that we consider the same number of equivalents of solute in each case. What we really wish to know is the *conductance per equivalent weight of solute.*

Consider a conductance cell of the type illustrated in Fig-

ure 2.1. The cell itself is constructed of some non-conductor such as glass. The two electrodes *A* and *B* consist of metal strips which fit closely between the sides of the cell. The top is open. *G* is a current-measuring instrument such as an ammeter or a galvanometer and should be very sensitive if we wish to measure very small currents. For very rough measurements a light bulb may be used instead of the ammeter. If a conducting solution is placed in this box and a voltage applied to the electrodes, any current which passes from *A* to *B* must pass through the solution. If a sugar solution is placed in this cell together with any additional amount of water, the mixture shows no appreciable conductance. The same is true of solutions of alcohol, ether, glycerine and many similar substances. On the other hand, if sodium chloride in water is placed in this cell, the solution is a very good conductor of electricity. Solutions of many solutes such as HCl, H_2SO_4, NaOH, and K_2SO_4 show a high conductance, while only a relatively small number of compounds give solutions which are slightly conducting.

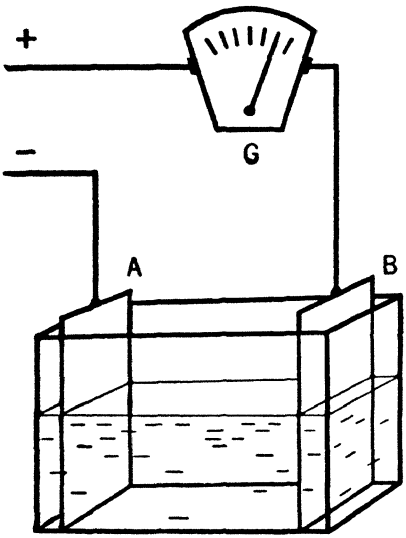


FIG. 2.1 Conductance cell and measuring instrument.

The great majority of solutions fall into one of two distinct classes, very good conductors and non-conductors. Substances the solutions of which are good conductors of electricity are called ***electrolytes,*** and substances that are non-conductors in solution, ***non-electrolytes.*** The difference in conductance shown by electrolytes and non-electrolytes is not merely a difference of degree. It is a *difference of kind.* If we were to classify all substances according to ability to conduct an electric current, we should find a great number which show

practically no conductance; almost all the rest show high conductance, with only a relatively few substances falling between these two classes. Were the difference between non-electrolytes and electrolytes one of degree rather than one of kind, we should expect most substances to show about the same conductance, with only a relatively few displaying very high conductance, and a very few, almost no conductance. Such would be the case if we were to consider the density rather than conductance of these same substances. The density of most substances lies between 2 and 5 grams per milliliter (or cubic centimeter). Very few substances have densities less than 0.6 gram per milliliter, and very few, greater than 18 grams per milliliter.

The difference of kind between strong and weak electrolytes suggests that there is a fundamental difference between the molecular structures of these two classes of substances. At a later time we shall show that our concept of molecular structure adequately explains this difference.

Variation of Conductance with Concentration. If 1 mole (gram formula weight) of an electrolyte such as sodium chloride is placed in the cell (Figure 2.1) together with 1 liter of water (the cell is not filled), a definite conductance will be observed. Upon the addition of more water, the solution will be diluted but the same amount of sodium chloride will remain between the plates. However, it is observed that the conductance is increased. The fact that the conductance increases with dilution may at first sight seem to be an anomaly, since by dilution the concentration decreases, but it must be borne in mind that we are not considering the conductance of a solution with a fixed cross section. As water is added to the cell the surface of the electrode exposed to the solution increases, as does the cross section of the conducting solution.

The conductance of an electrolyte increases with increasing dilution as shown in Figure 2.2. As the solution is diluted the concentration decreases (from right to left along the horizontal axis). After considering the next section on "The Lowering of the Freezing Point" we shall give an explanation of this phenomenon.

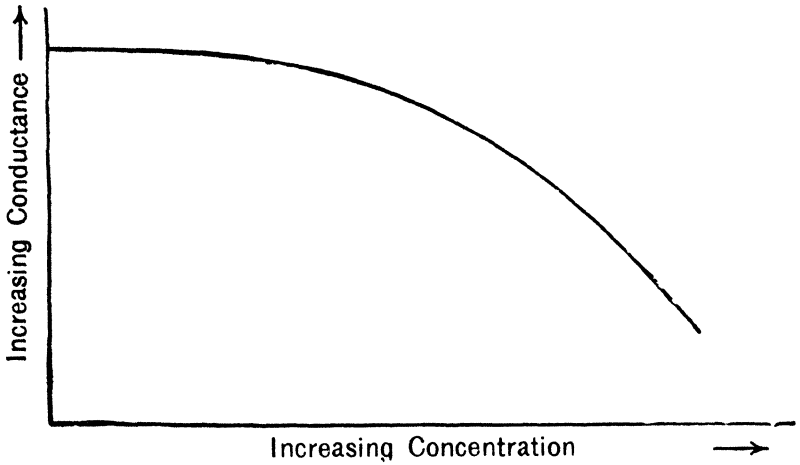


FIG. 2.2 Change in conductance with concentration.

The Lowering of the Freezing Point. The freezing point of water is lowered by the addition of a solute. The difference between electrolytes and non-electrolytes in this respect is well demonstrated in Table 3. The second column of the table gives the concentration of the solute in question in terms of moles or gram formula weights per liter of water, while the third column lists the freezing point lowering, i.e., freezing point of solution in degrees below 0° C.

We see that for non-electrolytes 0.1 mole of any substance dissolved in 1 liter of water lowers the freezing point about 0.186° C, and 0.2 mole per liter has twice this effect. It is to be observed that there is some variation in the effects of different solutes, but this variation is a relatively small one (methyl alcohol 0.181° C). The conclusion we can immediately draw is that the total number of moles per liter or the total number of molecules per liter of non-electrolytes is the principal determining factor in the lowering of the freezing point. The kind of molecule has little or no effect. If electrolytes behaved like non-electrolytes in solution, we should expect that their freezing point lowerings would be the same. More specifically, if sodium chloride in solution consisted of molecules, each of which contained one atom of sodium and one atom of chlorine, a gram formula weight would be the same as a mole and we

TABLE 3

FREEZING POINT LOWERING OF SOLUTIONS OF SUBSTANCES IN WATER

Substance (Non-electrolytes)	Concentration (Moles per liter)	Freezing Point Lowering
Glycerine	0.1	0.187
Glycerine	0.2	0.374
Ethyl alcohol	0.1	0.183
Methyl alcohol	0.1	0.181
Methyl alcohol	0.2	0.362
Dextrose	0.1	0.186
Dextrose	0.2	0.374
Cane Sugar	0.1	0.188
Hydrogen peroxide	0.1	0.184
Sugar 0.05 Glycerine 0.05	0.1	0.187
Average of a large number of non-electrolytes	0.1	0.186
Electrolytes		
HCl	0.1	0.352
KNO_3	0.1	0.331
KCl	0.1	0.345
NaCl	0.1	0.348
Na_2SO_4	0.1	0.434
$CaCl_2$	0.1	0.494
$NiCl_2$	0.1	0.538

should expect that the lowering of the freezing point would be the same as for non-electrolytes. Instead the lowering of the freezing point for HCl, KNO_3, KCl, and NaCl is almost twice that for non-electrolytes; and for Na_2SO_4, $CaCl_2$, and $NiCl_2$ more than twice and almost three times that of non-electrolytes. Again we see a difference in kind between electrolytes and non-electrolytes.

Interpretation of the Foregoing Facts by the Theory of Ionization. Our problem is to interpret the fact that electrolytes give a greater lowering of the freezing point — almost two and sometimes three times as great as that of non-electrolytes. In a general way, we already know the answer — the theory of ionization — yet let us follow the logic of the argument to determine what the assumptions are and to judge the justification of any conclusions we may draw. In order to explain the fact that the lowering of the freezing point of some electrolytes like NaCl is almost twice that for non-electrolytes, we assume that the electrolyte is present in the solution as ions, not as molecules. If sodium chloride existed in solution as uncharged molecules of NaCl we should expect a lowering of the freezing point of 0.186° per 0.1 formula weight. Twice this lowering would mean twice as many particles, which effect could be explained only by the presence of sodium and chlorine particles existing separately in solution. Since a solution of sodium chloride is a good conductor we also assume that the particles are charged; one kind to be positively charged and one kind negatively charged.

In a general way the explanation seems to be a satisfactory one. However, we may ask why the lowering of the freezing point of sodium chloride and similar substances is not more nearly twice that of non-electrolytes. There are two possible ways of explaining this latter fact. Let us consider a 0.1 molal solution (0.1 formula weight per 1000 grams of water — refer to page 17) of sodium chloride as an example. For this solution the freezing point lowering is 0.348° C. If all the sodium chloride existed as Na^+ and Cl^- ions we would expect the freezing point lowering to be $2 \times 0.186°$ or 0.372° C, *if ions behaved exactly like neutral particles or molecules in solution.* If ions behaved like molecules in solution we can calculate that about 13 percent of the Na^+ and Cl^- ions are united in the form of uncharged NaCl molecules, i.e., 87 percent of all the sodium chloride in a 0.1 *M* solution is in the form of ions and 13 percent in the form of molecules.

How does this explanation apply to the experimental results

of conductance? If the assumption that only part of the sodium chloride (87 percent) is in the form of ions is valid, then we should expect that at very great dilutions all or almost all of the sodium chloride would be in the ionic form, for at great dilutions the ions would be relatively far apart and would not have the same chance of combining with each other to form molecules. The molar or equivalent conductance would therefore increase with increasing dilution, as it does. If further we assume that ions move with the same velocity in dilute as in the more concentrated solutions, then the conductance of a 0.1 *M* sodium chloride solution should be 87 percent of that of an exceedingly dilute one. As a matter of fact the conductance is about 90 percent that of the very dilute solution. The agreement between experiment and prediction, in this case, is not perfect but good enough to have led chemists to this view, which they retained over thirty years. Today the idea of partial ionization of *strong* electrolytes is no longer considered tenable in spite of the reasonable agreement referred to above. Chemists now regard practically *all* the sodium chloride in 0.1 *M* solution to be present as ions, not to the extent of 87 percent or 90 percent, but *100 percent as ions.* How then are we to explain the fact that the lowering of the freezing point is not $2 \times 0.186°$ instead of 0.348° and how are we to explain the increased conductance of sodium chloride with increasing dilution?

Let us first get a picture of what we mean by the sodium ion or chloride ion in solution. The sodium ion is designated by the symbol Na^+ and from this it might be inferred that we believe that the sodium ion exists alone and unattached to other molecules in the solution. Evidence from conductance experiments tells us, however, that the sodium ion has several molecules of water quite firmly attached to it. The number is somewhat variable and is dependent upon the concentration of the sodium chloride and upon the temperature of the solution. From what we said previously regarding the polarity of water molecules we might expect such a process to take place. We might expect that the negative ends of the water molecules

would be attached to the positive sodium ion and form a blanket around it. Such a condition is illustrated in Figure 2.3. The same concept is held for the negative chloride ion and in general for all ions.

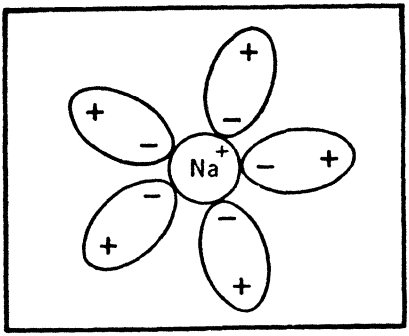


FIG. 2.3 Concept of the hydrated Na^+ ion.

Let us now examine closely the assumptions made in drawing conclusions regarding the partial ionization of sodium chloride to determine, if possible, the weak point of the argument. Two assumptions were implicitly made: (1) that charged particles (ions) behave like neutral molecules in lowering the freezing point of water and (2) that ions under the influence of an electric field move with the same velocity in the dilute as in the more concentrated solutions. Contrary to the first assumption we might expect that ions in solution with their greater attractions for the polar molecules of water would not behave exactly like neutral molecules. The second assumption does not seem reasonable, since a positive ion will certainly be hindered in its movement toward the negative electrode by the proximity of negative ions. The negative ions will act as a "drag" upon the positive ions and vice versa, tending to retard them. For this reason alone we should expect the conductance of concentrated solutions to be less than that of dilute solutions.

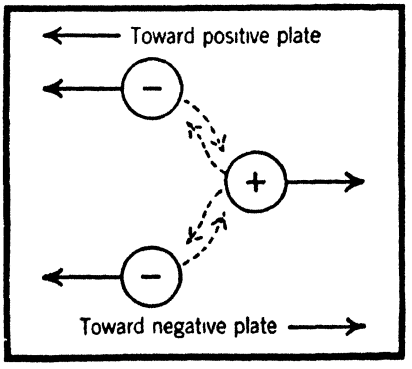


FIG. 2.4 The attractive force between the ions prevents easy flow.

The concept of ionic conductance and the effect of the close proximity of oppositely charged ions is illustrated in Figure 2.4.

The attractive force between positively and negatively charged particles tends to keep them near each other and to prevent the easy flow of these ions when they are placed between the two charged plates of a conductance cell. The nearer the particles are to each other (the more concentrated the solution), the greater is this hindrance to flow, or the greater the "drag-effect" becomes.

We can assume that the lowering of the conductance with increasing concentration is entirely due to this "drag-effect" and that the molecules are completely dissociated. Further evidence in support of the theory of complete dissociation is presented in Chapter 3. Evidence which we cannot present here has further strengthened this view until it has become almost universally accepted by chemists. Therefore we shall consider most strong electrolytes to exist in solution entirely in the form of ions.

Of all the common acids that we encounter in the laboratory, H_2SO_4, HNO_3, and HCl are 100 percent ionized (strong). All other common acids are partially ionized (weak). The hydroxides of the alkali and alkaline earth metals are strong bases. All salts are strong electrolytes with the exception of the halides of zinc, cadmium, and mercury and a few of the salts of lead.

There are other arguments which support the theory of ionization, as it was first proposed by the Swedish chemist, Arrhenius. These include the transfer of matter by electricity in solutions of electrolytes, Faraday's Law which was used to assign the number of charges on each ion, and the common color of the same ion in solutions of different salts. A consideration of these phenomena may be found in almost any textbook of general chemistry.

The Solubility of Electrolytes in Water. In considering the solubility of electrolytes we must first regard the substances in solution to be in the form of ions and not molecules. Experiment supports the view that in the crystal form the electrolyte also exists as positive and negative ions regularly arranged with respect to each other. The sodium chloride

crystal, for example, is built up of sodium ions and chloride ions, alternately spaced in such a way that each sodium ion is surrounded by six negative chloride ions and each chloride ion by six positive sodium ions. The difference in state between the ions in the crystal and those in solution is the close regular packing in the crystal and the hydration as well as random distribution of the ions in solution. The process of solution of sodium chloride is given in Figure 2.5. The positive

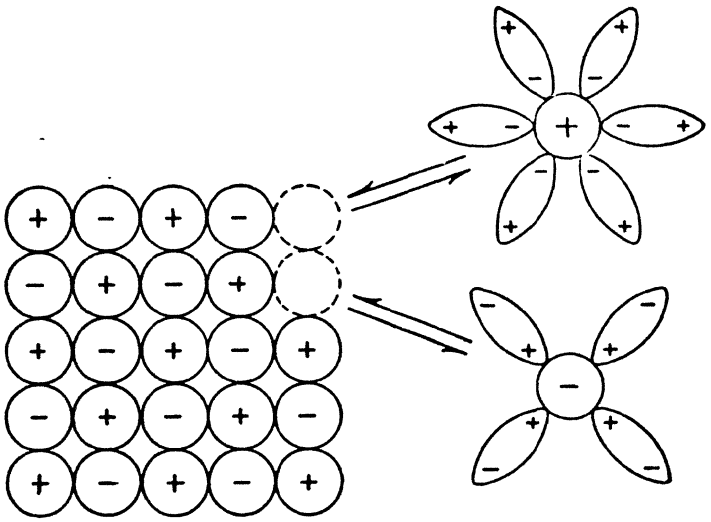


FIG. 2.5 Schematic view of the process of solution and crystallization of sodium chloride.

sodium ions leave the crystal and become surrounded by the polar water molecules, and the same is true of the negative chloride ions. The ions are said to be hydrated. The same number of chloride ions as of sodium ions enters the solution but nowhere is it necessary to assume that the sodium and chloride ions leave the crystal as molecules. The same picture would apply to the reverse process, that of precipitation.

Whether any electrolyte is soluble or only slightly soluble will depend upon the nature of the competition for its ions. If the forces of attraction of the ions for each other are great

in the crystal, the solubility will necessarily be less, but if the tendency of the water molecules to hold the ions is great, the solubility will be increased. To say that a substance is very soluble means, according to our concept, that the crystal forces are small and that the attractive forces of the water molecules for the ions are great. Hydrated ions may be regarded as having some similarity to water molecules, since they have water molecules attached to them.

Weak Electrolytes. Inasmuch as any strong electrolyte is to be regarded as completely ionized, its conductance in water solution will be equal to the sum of the conductances of its individual ions. For example, the conductance of a solution of sodium chloride is equal to the conductance due to the Na^+ ion plus the conductance due to the Cl^- ion. If in very dilute solution all ions were to move independently of each other and with the same velocity when subjected to the same conditions, it would follow that the equivalent conductance values of all electrolytes would be identical. Since the conductance values are not the same for all electrolytes of the same type we must conclude that some ions travel faster than others. Thus it might be expected that the light and small H^+ ion would travel faster than the heavy and large Cs^+ ion.

In very dilute solutions we might expect that the "drag-effect" would be inappreciably small and that, when subjected to the same electric field (same voltage per centimeter length of cell), each ion would move with a definite velocity which is independent of the nature of the ion with which it is associated. For example, the chloride ion would move with the same velocity in a dilute solution of potassium chloride as it would in a dilute solution of sodium chloride. In other words, the conductance contributed by the chloride ion is the same in both solutions.

However, in solutions of potassium chloride and sodium chloride the sodium ion would not travel with the same velocity as the potassium ion, nor would either of these ions necessarily travel with the same velocity as the negative chloride ion. At

first sight it may be confusing to have a condition in which positive and negative ions travel with different velocities. One might argue that positive or negative ions would accumulate at one end of the conductance cell. It must be borne in mind that reactions take place at the electrodes which will offset to a large extent any such accumulation and keep the number of positive and negative charges practically the same in all parts of the cell.

Let us assume that in dilute solution the ions are independent of each other in their current-carrying capacities, and follow the method of determining the conductance of nitric acid from the conductance values of solutions of sodium nitrate, sodium chloride, and hydrochloric acid. Let us imagine that we are using a cell such as that described on page 26 and that in all of the experiments we impose the same potential between the two electrodes. Under these conditions the current carried by any electrolyte is proportional to its conductance. We shall designate the current carried by one equivalent of any substance as Λ. Since sodium nitrate is completely ionized, the current carried by this substance is equal to the current carried by the sodium ion plus the current carried by the nitrate ion.

$$\Lambda(NaNO_3 \text{ soln.}) = \Lambda(Na^+) + \Lambda(NO_3^-) \quad (1)$$

$$\Lambda(HCl \text{ soln.}) = \Lambda(H^+) + \Lambda(Cl^-) \quad (2)$$

By adding these two equations we obtain the conductance of a solution containing one equivalent each of sodium nitrate and of hydrochloric acid. The total conductance is the sum of the conductances of all four ions.

$$\Lambda(NaNO_3 + HCl \text{ soln.}) = \Lambda(Na^+) + \Lambda(H^+) + \Lambda(NO_3^-) + \Lambda(Cl^-) \quad (3)$$

If we could remove the sodium and chloride ions from this solution, a solution of nitric acid would be left. However, it is not necessary to remove these ions to obtain the conductance of a solution containing H^+ and NO_3^- ions. Since the conductance of a solution of sodium chloride is

$$\Lambda(NaCl \text{ soln.}) = \Lambda(Na^+) + \Lambda(Cl^-) \quad (4)$$

we need only subtract equation (4) from equation (3) to obtain the desired result, $\Lambda(H^+) + \Lambda(NO_3^-)$, which is equal to the conductance of a dilute solution of nitric acid. Making this calculation quantitatively, we find that the value so calculated for the conductance of a nitric acid solution agrees with that obtained experimentally. Thus we have evidence that our assumption regarding the independent movement or current-carrying capacity of the ions is a reasonably valid one when applied to dilute solutions.

In the same way we can calculate the conductance that a solution of acetic acid (HAc) would have if it were a strong electrolyte. This is the sum of the conductances of the hydrogen and acetate ions, which we can determine in the following manner:

$$\Lambda(\text{NaAc soln.}) = \Lambda(Na^+) + \Lambda(Ac^-) \quad (5)$$

$$\Lambda(\text{HCl soln.}) = \Lambda(H^+) + \Lambda(Cl^-) \quad (6)$$

$$\Lambda(\text{NaCl soln.}) = \Lambda(Na^+) + \Lambda(Cl^-) \quad (7)$$

Adding equations (5) and (6) and subtracting (7) we obtain

$$(5) + (6) - (7) = \Lambda(H^+) + \Lambda(Ac^-) \quad (8)$$

The value so calculated would be the conductance of a dilute acetic acid solution *if acetic acid were completely ionized.*

Comparing the value for the conductance of an acetic acid solution, as calculated above, with that determined experimentally for a 0.1 *M* solution, we find that the experimentally determined conductance is only about 1 percent of the value calculated. The value of the conductance of a 0.1 *M* sodium chloride solution is about 90 percent that for a very dilute solution. This fact we explained by the "drag-effect" due to the attractions of the positive and negative ions for each other. With acetic acid, however, the ratio of the conductance of a 0.1 *M* solution to that of a very dilute solution is of another order of magnitude (1 percent) and we cannot explain this in the same way. We must now assume that acetic acid exists in solution chiefly as acetic acid molecules and that only about 1 percent of these molecules is dissociated into hydrogen

and acetate ions. There are quite a number of substances, particularly organic acids and bases, which are only partially ionized. Such substances are known as ***weak electrolytes*** and are intermediate between non-electrolytes and strong electrolytes. While such substances are not as numerous, by any means, as either the ***strong electrolytes*** (sodium chloride type) or as the non-electrolytes, they are nevertheless a very important class of substances with which we shall be very much concerned.*

The Use of Ionic Equations. If a solution of sodium hydroxide is neutralized by one of hydrochloric acid the resulting solution will be one of sodium chloride. The hydroxide ion, OH^-, of the sodium hydroxide solution reacts with the hydrogen ion of the hydrochloric acid solution to produce water; no reaction takes place between the sodium and the chloride ions. If the equation we are to use to represent the change taking place in this reaction is to include only those substances which disappear and those which are formed, we may express the above change by

$$H^+ + OH^- = H_2O \qquad (9)$$

Some prefer to express this change as

$$HCl + NaOH = NaCl + H_2O \qquad (10)$$

or if the substances involved are to be expressed as ions,

$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O \qquad (11)$$

In the last equation the ions Na^+ and Cl^- appear on both sides and may be cancelled to give equation (9).

Equation (9) does not give information as to what particular kind of solutions were used, since the neutralization of solutions of potassium hydroxide and nitric acid would be ex-

* The terms ***strong*** and ***weak*** must not be confused with ***dilute*** and ***concentrated.*** A strong electrolyte is completely or almost completely ionized in solution, while a weak electrolyte is ionized to only a small extent. A concentrated solution is one which contains a relatively large amount of solute per unit volume, regardless of whether the solute is strong, weak or a non-electrolyte. A dilute solution contains a relatively small amount of the solute.

pressed by the same equation. On the other hand, the use of the simple equation (9) includes only those substances that enter into the reaction and gives the information that strong electrolytes are involved. *This equation also tells us that the substances involved are in solution.* If gaseous hydrogen chloride were to react with solid sodium hydroxide to give steam and solid sodium chloride, the equation for the reaction would be more properly expressed by (10). Furthermore, when we come to deal with equilibria and the corresponding equilibrium constants for chemical reactions, we shall find that equations such as (10) and (11) have to be interpreted in terms of ionic equations such as (9). Ionic equations are conventional, as well as expressions of the net result of ionic reactions, and we shall use such equations whenever ions are involved in the reactions.

Some chemists prefer to indicate the hydration of the ions in the equation for the reaction, then to consider these reactions from a somewhat different point of view (a point of view which we shall consider more fully in a later chapter). This school would indicate the H^+ ion as H_3O^+ (the hydronium ion), i.e., the H^+ ion as attached to one molecule of water. Under this system equation (9) would be written as

$$H_3O^+ + OH^- = 2H_2O \qquad (12)$$

For the most part we shall not follow this system but rather indicate the formulae of the ions in their simplest forms, always bearing in mind that the ions are all hydrated.

The equation for the neutralization of a solution of acetic acid (HAc) by a solution of sodium hydroxide, we write as

$$HAc + OH^- = H_2O + Ac^- \qquad (13)$$

Here we write acetic acid as HAc and not as H^+ for in this case most of the acetic acid in solution is in the form of molecules and not in the form of ions. It is the molecules of acetic acid which ultimately disappear in the reaction, so it is necessary to designate them as such and to include them in the equation.

Likewise, the formation of silver chloride by the addition of a solution of silver nitrate to one of sodium chloride is written

$$Ag^+ + Cl^- = AgCl(solid) \qquad (14)$$

In this reaction only the silver and chloride ions and the precipitated silver chloride are involved; the sodium and nitrate ions take no part in the reaction whatsoever; they contribute neither to the forward nor to the reverse reaction.

Questions and Problems

1. What is the difference between an electrolyte and a non-electrolyte?
2. By what reasoning can we come to the conclusion that there is a sharp difference between electrolytes and non-electrolytes (e.g., a difference of kind)?
3. Is the equivalent conductance (conductance of 1 gram formula weight) of sodium chloride in solution increased or decreased if the solution is diluted with water?
4. What is the average lowering of the freezing point of water if 0.1 mole per liter of a non-electrolyte is added to it?
5. What would be the freezing point of a solution which contains .05 mole of sugar, .05 mole of glycerine and .05 mole of alcohol, all in 1 liter of the same solution?
6. Explain why a dilute solution of sodium chloride has a greater conductance (per formula weight of NaCl) than does a more concentrated solution.
7. Do ions in solution behave like neutral molecules in their effect on the lowering of the freezing point?
8. Is a sodium chloride solution regarded as containing both sodium chloride molecules and the ions Na^+ and Cl^-? Explain.
9. What is the distinction between a strong acid and a concentrated one? Name three strong acids.
10. Give a schematic picture of the process taking place when solid sodium chloride dissolves in water.
11. Give an example of a weak electrolyte.
12. The equivalent conductance of a .01 molar solution of $NaNO_3$ at 25° C is 99 reciprocal ohms; that for a .01 molar solution of HCl, 391 reciprocal ohms; and for a .01 molar solution of NaCl it is 107 reciprocal ohms. Calculate the equivalent conductance of a .01 molar solution of HNO_3 and compare with the experimental value of 384 reciprocal ohms.

CHAPTER

3

The Structure of Atoms and Molecules

The concepts of polarity and of electrolytes and non-electrolytes, presented in the last two chapters as well as the concepts of valence and the stability of molecules can be pictured in greater detail and explained by considerations of the electronic structures of atoms and molecules.

To help us visualize atoms and molecules in our mind's eye and thus help us understand the phenomena of chemistry, we shall, in this chapter, devote our attention to this experimentally verified and accepted theory.

General Concepts. All the experiments of chemistry and physics are consistent with the view that atoms are built up of positively charged nuclei surrounded by negative electrons. The nucleus of the atom possesses a charge which is equal in magnitude to the total charge of all the electrons surrounding the nucleus. This charge is known as the ***atomic number*** of the atom.

To account for the classification of the elements into the main groups of the periodic system it is assumed that (1) the electrons in the atom are arranged in concentric shells; (2) the number of electrons in each shell is definitely limited; (3) the inner shells of an atom are filled while the outermost shell, except in the case of the rare gases, is not filled; and (4), the chemical properties of the atom depend upon the number of electrons in the outermost shell.

The charge on the nucleus, hence the number of electrons

surrounding it, increases by one unit in passing from one element to the next element of higher atomic weight. When the number of electrons in the outermost shell becomes filled, a new shell is begun. The first or innermost shell requires two electrons to fill it. The next outer shell requires eight electrons and the other shells still more. The electrons of the filled shells are so tightly bound that they cannot be loosened sufficiently to form chemical bonds. Atoms are attached to each other to form molecules through transfer of electrons from one atom to another, or through sharing of common electrons by two atoms. Since only the electrons of the outermost shell undergo such transfer or sharing and thus account for the chemical properties of the atom, our attention shall be largely confined to these electrons.

The Inert Gas Structures. As we all know, the inert gases do not form any compounds — a fact which was of great significance to the chemists and physicists who first formulated their ideas of atomic structure. Evidently there is something about their structures that makes them particularly stable; the stability of their electronic structures cannot be enhanced through combination with other atoms as is the case with other elements. The distributions of electrons in the various shells about the nuclei of these elements are given in Table 4 on page 43.

The number of electrons in each shell from the nucleus outward for any given atom is read horizontally. Thus the innermost shell (*K* shell) of radon contains 2 electrons, the next shell (*L* shell) 8 electrons, then 18, 32, 18, and finally 8. Note particularly that (1) with the exception of helium, each of the outermost shells of all these atoms contains 8 electrons; (2) each of these atoms has two electrons in the *K* shell and 8 in the *L* shell; and (3) the stable filled shells contain 2, 8, 18, or 32 electrons — these numbers are equal to 2×1, 2×2^2, 2×3^2, and 2×4^2, respectively.

The Structures of Group I. The main group I of the periodic table (see back cover) consists of H, Li, Na, K, Rb, Cs, and Fr. We shall consider the structures of these atoms

TABLE 4

ELECTRONIC STRUCTURES OF INERT GASES

Atomic Number	Element	Number of Electrons in Shell					
		K	*L*	*M*	*N*	*O*	*P*
2	Helium	2					
10	Neon	2	8				
18	Argon	2	8	8			
36	Krypton	2	8	18	8		
54	Xenon	2	8	18	18	8	
86	Radon	2	8	18	32	18	8

(*The designations K, L, M, etc., are arbitrary.*)

and note the differences between these and the structures of the inert gases.

TABLE 5

ELECTRONIC STRUCTURES OF GROUP I

Atomic Number	Element	Number of Electrons in Shell						
		K	*L*	*M*	*N*	*O*	*P*	*Q*
1	Hydrogen	1						
3	Lithium	2	1					
11	Sodium	2	8	1				
19	Potassium	2	8	8	1			
37	Rubidium	2	8	18	8	1		
55	Cesium	2	8	18	18	8	1	
87	Francium	2	8	18	32	18	8	1

Neglecting hydrogen, which we shall consider later, we see that, except for the single electron in the outermost shell, the structures are the same as those for the inert gases. Were these atoms to lose their outermost electrons through chemical reaction then they would revert to the stable structure of the inert gases. That is just what they do when they react to form

the ions Li^+, Na^+, K^+ etc. Nor would we expect any of them to lose another electron from the next shell to form doubly charged ions, since the inert gases do not do so.

The Electronic Structures of Group VII. Let us contrast the electronic structures of the electro-positive elements in Group I with those of the electro-negative elements of Group VII.

TABLE 6

ELECTRONIC STRUCTURES OF GROUP VII

Atomic Number	Element	Number of Electrons in Shells					
		K	*L*	*M*	*N*	*O*	*P*
9	Fluorine	2	7				
17	Chlorine	2	8	7			
35	Bromine	2	8	18	7		
53	Iodine	2	8	18	18	7	
85	Astatine	2	8	18	32	18	7

We note that each of these atoms has 7 electrons in the outermost shell. If each of them should acquire one electron to form a negative ion (for example, Cl^- ion), the structures of these negative ions would correspond to the stable inert gas structures as given in Table 4. It is well known, of course, that each of these elements forms singly charged negative ions. The positive elements lose electrons and the negative elements acquire electrons to form the stable inert gas structures.

Electronic Structures of the Second Series. As we proceed along any horizontal row (series) of the main group elements, in the periodic table, the core of the atoms considered remains the same, except for the nuclear mass and charge, and only the number of electrons in the outer shell changes. The core of the atom is to be distinguished from the nucleus in that it contains the nucleus and all the electrons except those in the outermost shell. The electronic structures for the second series are given in Table 7.

We should expect those elements on the extreme left side of this table (except Ne) to have a tendency to lose electrons, to revert to the neon structure, thus forming positive ions; and those elements on the right to acquire electrons, forming

TABLE 7

ELECTRONIC STRUCTURES OF THE SECOND SERIES

Element and Atomic Number	Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17
K shell	2	2	2	2	2	2	2	2
L shell	8	8	8	8	8	8	8	8
M shell	0	1	2	3	4	5	6	7

negative ions or negative valences and thus acquiring the stable argon structure. The chemical facts are in accord with these expectations.

Since it is only the outermost electrons that are of significance from a chemical standpoint, it has become customary to represent the electronic structure of an atom by its symbol surrounded by as many dots as there are valence or outside electrons. In such a case the symbol alone represents the core of the atom. Thus, $\dot{\text{N}}\text{a}$ represents the sodium atom, and $:\ddot{\underset{\cdot\cdot}{\text{Cl}}}\cdot$ the chlorine atom.

Compound Formation by the Transfer of Electrons. When equal numbers of sodium and chlorine atoms combine to form sodium chloride, a typical electrolyte, the one outermost electron of each sodium atom is taken up by the chlorine atom, thus forming in the crystal a symmetrical alignment of positively charged sodium ions and negatively charged chloride ions. A crystal of sodium chloride then consists, not of sodium and chlorine atoms, but of sodium and chloride ions. The electronic structures of these ions are shown schematically in one plane in Figure 3.1. Actually, the electrons are distributed in a spherical shell. Note in Figure 3.1 that each ion has an outermost shell of eight electrons complete in itself. Likewise,

when sulfur $\ddot{\underset{\cdot\cdot}{S}}$: combines with sodium $\dot{N}a$ we should expect the compound Na_2S to be formed, for the sulfur atom requires two electrons to form the stable group of eight electrons, and each sodium atom can contribute only one of these.

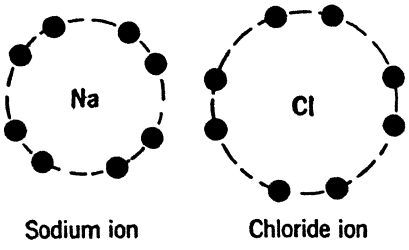


FIG. 3.1

We find that those compounds formed by the transfer of electrons (as contrasted with the sharing of electrons) are strong electrolytes.

The Sharing of Electrons and the Covalent Bond. Carbon tetrachloride, a non-electrolyte, consists of a carbon atom surrounded by four chlorine atoms. The carbon atom by itself has four electrons in the outermost shell. These can supply the vacancies in the outermost shells of the chlorine atoms in carbon tetrachloride, one electron for each chlorine. With the extra electron furnished by the carbon atom, each chlorine atom will have a completed group of eight electrons as its outermost shell. But the carbon atom also must have eight electrons surrounding it, so two electrons must be shared by it and by each chlorine atom. That is, the carbon atom contributes four electrons and each chlorine atom one of its seven electrons to make a total of eight electrons about the carbon. All of these electrons then are shared between the carbon and the chlorine. This condition is illustrated in Figure 3.2.

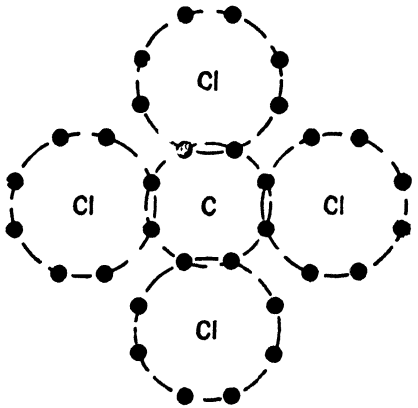


FIG. 3.2 Electronic structure of carbon tetrachloride.

The electronic structure of methane, another non-electrolyte, is shown in Figure 3.3. In this case each hydrogen atom

supplies one electron and the carbon four electrons. These electrons are shared by both the hydrogen and carbon. There are only two electrons for each hydrogen atom but this is also a rare gas structure, that of helium.

Iodine chloride is a compound of iodine and chlorine having the formula ICl. Both the chlorine and the iodine atoms have seven electrons in the outermost shell, and to produce an electronic structure for which each atom has eight electrons surrounding it, it is necessary that two electrons be shared by the two atoms in question. The structure of this compound is given in Figure 3.4.

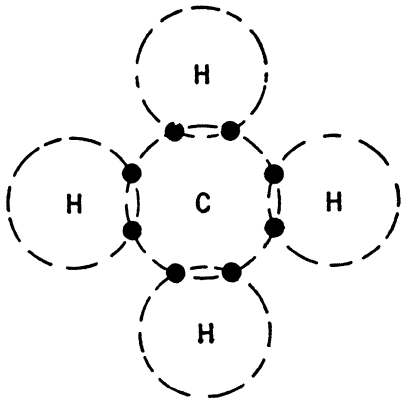


FIG. 3.3 Electronic structure of methane.

By referring to both Figures 3.1 and 3.4, the difference between electrolytes and non-electrolytes becomes apparent. Each atom of an electrolyte has a group of eight electrons about it which has been completed without the necessity of sharing any of these electrons with any other atom. The atoms of non-electrolytes are bound together by shared electrons. When electrolytes dissolve in water the ions can separate and still retain the group of eight about each ion. The atoms of non-electrolytes are held together so strongly by the shared electrons that they cannot easily exist as separate ions. If iodine chloride were to dissociate in solution to produce one positive and one negative ion it would be necessary for the positive ion to have but six electrons about it. Such a condition is not necessary for the

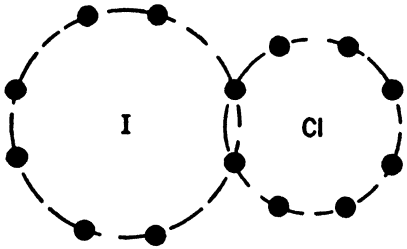


FIG. 3.4 Electronic structure of iodine chloride.

production of Na^+ and Cl^- ions. Iodine chloride, since it is a compound produced by the sharing of electrons, is not an electrolyte.

Sodium sulfate is an electrolyte which exists in solution as sodium ions, Na^+, and sulfate ions, SO_4^{--}. The sulfate ion does not dissociate into smaller fragments for it is held together by shared electrons. Its structure is shown in Figure 3.5. The sulfate ion, however, does not require the sharing of two of its electrons with each sodium particle and therefore it can exist by itself in solution as an ion. The sulfur and oxygen atoms belong to the sixth group of the periodic system and therefore each furnishes to the whole structure six valence or outside electrons. These five atoms then furnish thirty electrons but thirty-two are necessary for all the groups of eight shown in Figure 3.5. The two additional electrons are furnished by the atoms with which this radical is associated in the particular compound in question; for example, the two sodium atoms supply these in the compound Na_2SO_4, thus forming two sodium ions, and the two additional electrons on the sulfate ion produce a charge of -2. The sulfate ion is to be regarded as a unit with completed electronic structure. The oxygen atoms are held to the sulfur atom by shared electrons. This shared electron structure accounts for the stability of the sulfate ion; there is little tendency for the oxygen atoms to break away from the sulfur atoms. If this process were to take place, the groups of eight electrons shown in Figure 3.5 would be broken up.

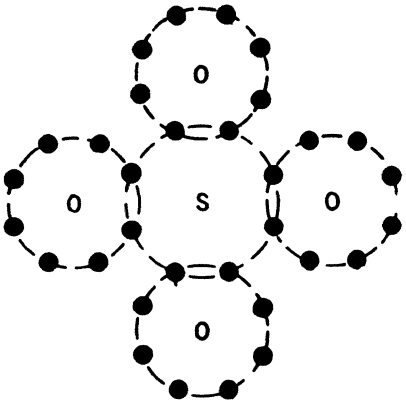


FIG. 3.5 Electronic structure of the sulfate ion (dotted circles indicate completed shells).

The difference between electrolytes and non-electrolytes lies in the difference between the electronic structures of these two types of compounds; electrolytes involve the transfer of elec-

trons and non-electrolytes the sharing of electrons, to form the stable inert gas structures.

The Neutron — Hydrogen Atoms in Combination Form both Neutron and Helium-like Structures. The neutron is one of the fundamental atomic building blocks of nature. It consists merely of a nucleus with zero charge and no outside electrons, and its mass is very nearly the same as that of the hydrogen atom. Because of the lack of charge on the nucleus and because of its small size (no outer electrons), this particle has the ability to pass through thick blocks of lead, as well as other substances, with very little probability of being stopped. It is only stopped by collisions with the nuclei of other atoms, and since the nuclei are also exceedingly small, such collisions are of improbable occurrence.

The neutron may be regarded as an atom of an *inert gas* which lies above helium in the zero group of the periodic system. The neutron and hydrogen together then constitute the first series of the periodic system. With this concept, the first three series of the periodic system are

n	H						
He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl

By sharing two electrons with another atom, the hydrogen atom shows its tendency to form the helium-like structure. In the compound LiH, lithium hydride, the hydrogen atom displays this tendency in a more marked fashion, for this compound in the molten state is in the form of Li^+ and H^- ions, as may be shown by electrolysis.

When the hydrogen atom shows its tendency to revert to the neutron-like structure (no outside electrons), it forms a hydrogen ion.

In some combinations, such as methane, hydrogen shares electrons with the carbon atom. In acetic acid three of the hydrogen atoms are held to a carbon atom by electron sharing; the hydrogen is in the helium-like state. The hydrogen atom attached to one of the oxygen atoms behaves as though it shows

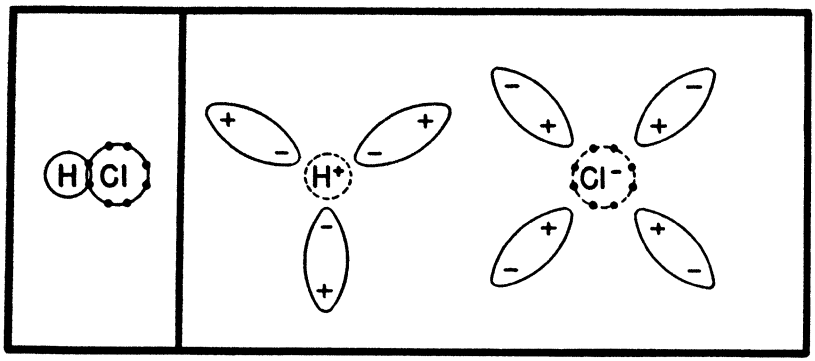


FIG. 3.6

A. Hydrogen chloride molecules in the liquid state. Hydrogen takes helium-like structure.

B. Hydrogen chloride in solution. Hydrogen displays neutron-like structure.

the tendency to form both the helium-like and the neutron-like structure, for only part of these hydrogen atoms bound to oxygen in the acid molecule form H^+ ions by dissociation.

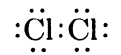
Liquid hydrogen chloride (*B.P.* $-85°$ C) is not a good conductor of electricity. In this form it is not ionized as H^+ and Cl^- ions. The hydrogen and chlorine atoms are to be regarded as being attached to each other by electron sharing. When the molecules of hydrogen chloride are placed in water, however, the attraction of the water molecules for both the H^+ and Cl^- ions changes this tendency on the part of the hydrogen atoms, and they all revert to the neutron structure.

For the purpose of explaining this dual behavior of hydrogen, the neutron is regarded as a rare gas atom.

Explanation of the Polarity of Molecules. In discussing polar molecules in a previous section in this chapter, no insight was given as to the reason for the differences between the polarities of various kinds of molecules. Our concept and theory regarding electronic structure offer an explanation of this phenomenon. To understand this problem we must bear in mind that the seat of the positive charge of an atom lies in the nucleus, while the electrons about the nucleus constitute the negative charge.

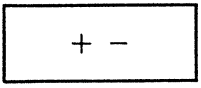
Let us first consider the neon atom and deduce from our concept of its structure whether neon is a polar or a non-polar substance. The charge on the nucleus is + 10 and there are a total of ten electrons in the two shells about the nucleus. The negative charge is symmetrically spaced about the positive charge and therefore there is no portion of the atom that contains more positive or negative charge than the diametrically opposite portion. The atom is therefore non-polar.

The chlorine molecule, the electronic formula of which is given four lines below, is made up of positive and negative charges symmetrically spaced. One chlorine atom is no more positively charged than the other. This substance is likewise non-polar.



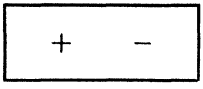
Chlorine Molecule

However, suppose one chlorine atom of the chlorine molecule is replaced by one iodine atom, we then have the molecule ICl, iodine monochloride. In this case the chlorine atom has a greater attraction for electrons than does the iodine atom and consequently a slightly greater negative charge exists about the chlorine than about the iodine atom. One end of the molecule is therefore slightly more negatively charged than the other and the molecule is slightly polar. The torque or turning effect of this molecule in an electric field would be equivalent to a positive and negative charge separated by only a small distance, and pictorially or schematically we may represent the polarity by a positive and negative charge rather close to each other, as shown in the following figure.



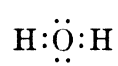
Sodium chloride, as we have said, does not form molecules consisting of one atom or ion of chlorine and one of sodium either in the solid state or in solution. In the gaseous state, however, the sodium chloride molecule does consist of one particle of chlorine and one of sodium. As previously stated,

the sodium atom has a tendency to give up one electron and the chlorine atom displays a tendency to acquire an electron. Therefore, in the gaseous NaCl molecule we should expect that portion of the molecule occupied by the sodium to be positively charged and that portion occupied by the chlorine atom to be negatively charged. The molecule should therefore be polar with the positive and negative charges separated to a greater extent than in the ICl molecule. Schematically we might represent such a polar molecule by



A relatively large effective distance exists between the charges.

The water molecule is a highly polar one. The polarity on the part of this molecule gives us some insight into its structure. If the water molecule consisted of two hydrogen atoms and an oxygen atom all arranged in a straight line, such as



it should display no polarity, for all positive and negative charges would be symmetrically distributed about the oxygen atom. Since the water molecule is polar, we can conclude that the above symmetrical structure is impossible. Rather, the structure of this molecule is that represented by the formula given in Figure 3.7. The bond angle between the hydrogen atoms is 105°. Since the oxygen atom tends to hold electrons more tightly than the hydrogen atoms, that portion of the molecule containing the oxygen atom would be more negatively charged than that containing the two hydrogen atoms.

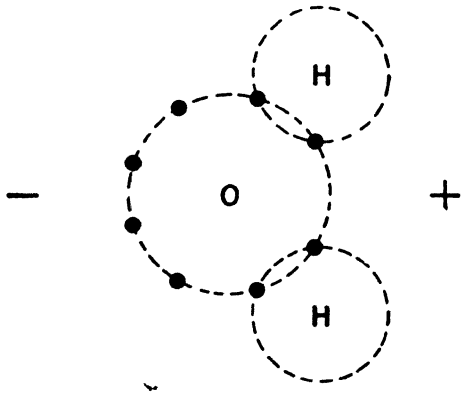


FIG. 3.7 Water molecule.

In general, if one atom in a molecule has a greater tendency to hold electrons than any of the others, the molecule will tend to be polar unless it is symmetrical. In CCl_4, for example, the chlorine atoms are negatively charged with respect to the carbon atom but the four chlorine atoms are symmetrically placed around the carbon atom and no polarity results. Chloroform, $CHCl_3$, on the other hand, does display polarity because of lack of symmetry.

The Hydrogen Ion in Water Solution — The Hydronium Ion. The hydrogen ion or proton is unique among positive ions in that it has no valence electrons and like the neutron is very small. Like other ions it is hydrated in solution, i.e., surrounded by polarized water molecules, but because of its small size and because the water molecule also contains protons, it is assumed that for the most part the hydrogen ion does not exist in the uncombined form in water solution. Through a regular chemical binding (i.e., an electron pair) the proton may attach itself to a water molecule to form H_3O^+. This singly hydrated hydrogen ion is known as the ***hydronium*** ion. This ion behaves like any other positive ion in that it is also to be regarded as one which is surrounded by polarized water molecules.

The hydronium ion is the analog of the well-known ammonium ion. Liquid ammonia, NH_3, has many properties common to water. Like the water molecule the ammonia molecule is polarized, and like water ammonia dissolves many salts to form conducting solutions. If a pure acid is added to liquid ammonia, the NH_4^+ ion is produced. A typical reaction is

$$NH_3 + HNO_3 = NH_4^+ + NO_3^- \qquad (1)$$

By analogy we may argue that the proton in solution is not H^+ but H_3O^+. The addition of a pure acid to water would give the analogous reaction

$$H_2O + HNO_3 = H_3O^+ + NO_3^- \qquad (2)$$

The electronic structures of both the ammonium ion and the postulated hydronium ion are given in Figures 3.8 and 3.9,

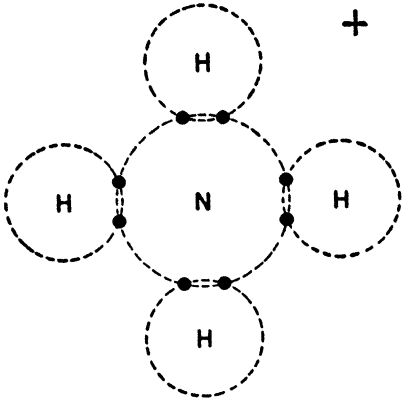


FIG. 3.8 The ammonium ion.

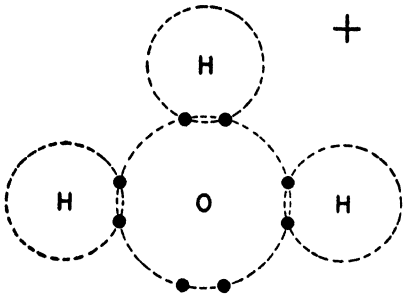


FIG. 3.9 The hydronium ion.

respectively. In the structure for the hydronium ion it is apparent that all three hydrogen atoms (or ions) are to be regarded as being alike, and that any one of the three can be removed. It should be pointed out, however, that these three hydrogen atoms are not in the same condition as are the two hydrogen atoms in the water molecule. The removal of one hydrogen ion from the hydronium ion results in the return of the two remaining hydrogens to their former condition. For example, if metallic zinc is placed into a solution containing hydronium ion (HCl solution), only one of the three protons is liberated as hydrogen gas. By the removal of one of these water is left, which we know does not react with metallic zinc.

With this concept the process of neutralization becomes one of competition between the water molecule and the OH^- ion for the proton. The OH^- ion has the greater affinity for the proton and therefore robs the H_3O^+ ion of it. The reaction for neutralization is

$$H_3O^+ + OH^- = 2H_2O \qquad (3)$$

Both the hydronium and hydroxide ions are hydrated in solution but this excess hydration is not represented in their formulae.

We may regard the reactions involving the hydrogen ion from two points of view: (1) the *transfer* of protons from water

molecules to other proton acceptors, and (2) the *addition* of hydrogen ions (protons) to acceptors (such as OH^- ion, Ac^- ion, etc.). The latter viewpoint is the one which has been accepted for many years. It recognizes that the proton is hydrated and in solution may exist in the non-hydrated form, H^+, the singly hydrated form, H_3O^+, the doubly hydrated form, $H_5O_2^+$, and possibly in forms of higher degrees of hydration. All these forms have been lumped together as "the hydrogen ion," having the simple symbol H^+. According to the Brønsted * viewpoint it is assumed that the amount of unhydrated H^+ ion is extremely small and that the singly hydrated form, H_3O^+, is the principal species present in any water solution. There are a number of pieces of information derived from experiments that give emphasis to the viewpoint that the H_3O^+ ion is the predominant species.

Throughout this text we shall continue to use the simplified concept and to indicate the hydrogen ion in solution merely by the symbol H^+, except in those places where the material in question is re-interpreted in terms of these newer definitions. As we shall see, this concept has some distinct advantages, but we shall retain the older definitions inasmuch as they have been used in the development of almost the whole of modern chemistry. As this course progresses we shall find it profitable to compare these two points of view.

The Sub-groups. In our previous discussion of electronic structure we have considered only the elements of the main groups of the periodic system. The electronic structures of these elements are all characterized by their close relationship to the structures of the inert gases. The sub-groups of the periodic system have structures which are not closely related to those of the inert gases, and this difference between the structures of the main and sub-groups accounts for the differences in their properties. To illustrate, let us consider sub-

* Johannes Nicolaus Brønsted (1879–1947), a Danish physical chemist, formerly Director of the Physico-Chemical Institute at Copenhagen, introduced new definitions and a new concept of acids and bases. These definitions will be developed at the appropriate places in the following chapters.

group one, the elements of which are Cu, Ag, and Au. Like the elements of the main group, Li, Na, etc., these elements display a valence of +1, but there the similarity stops. The metals of the main group are very reactive. Those of the sub-group are, on the contrary, inactive; they display more than one valence; and they readily form complex ions. The electronic structures for these elements are given in Table 8.

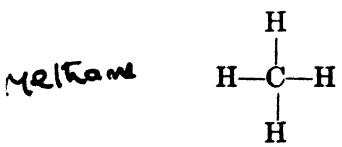
TABLE 8

ELECTRONIC STRUCTURES OF SUB-GROUP I

Atomic Number	Element	Number of Electrons in Shell					
		K	*L*	*M*	*N*	*O*	*P*
29	Copper	2	8	18	1		
47	Silver	2	8	18	18	1	
79	Gold	2	8	18	32	18	1

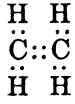
A comparison of Table 8 with Table 5 shows that the core of the main group elements is that of a rare gas and the core of those in the sub-group is not. The shell next to the valence shell in the sub-group elements contains 18 instead of 8 electrons and the electrons in this shell of 18 are not as tightly bound as those in the group of 8. Therefore one or two of these may act as valence electrons, thus accounting for the formation of the ions with valences greater than plus one. We shall have more to say about these structures in a later chapter.

Resonance and the Double Bond. From the foregoing considerations, it is apparent that a pair of electrons constitutes the single bond, as commonly designated by a single line. Thus, the usually designated structure for methane is

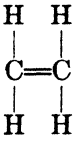


instead of that shown in Figure 3.3. Each line in this structure represents a pair of electrons. Since the use of electronic structures for molecules is cumbersome, we use these lines to indicate bonds, always bearing in mind that each bond represents a pair of shared electrons. Instead of representing the structure of ethylene as

ethylene



we indicate this merely as



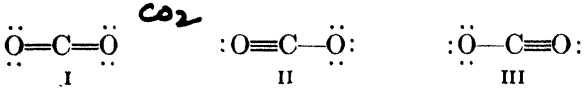
Sometimes it will be convenient for us to use both conventions, particularly in cases for which we wish to indicate in the structure the outer electrons which are not shared.

For example, the structure for the oxygen molecule may be indicated in two forms:

oxygen (A)  , or (B) 

From what we have said regarding the tendency of electrons to form rare gas structures we should expect the structure of oxygen to be that of (B). However, this is not the case, for the magnetic properties of the oxygen molecule indicate that two unpaired electrons are present in the molecule; therefore (A) is the predominating form. Actually, both forms exist. Oxygen is one of the relatively few molecules that break our rules. The electrons in the oxygen molecule are constantly shifting between the two forms, spending most of their time in form (A). This phenomenon of shifting between two forms we call *resonance.*

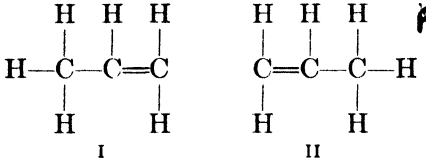
Another example of resonance is that of carbon dioxide. In this case there are three possible forms, each with rare gas structures about the carbon and oxygen atoms.



I II III

Calculations indicate that I is the most stable and therefore the predominating form, but all three forms exist. The electrons are shifting between these forms. The CO_2 molecule is in a state of resonance.

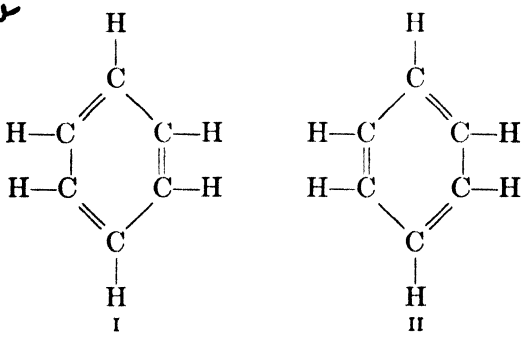
One might think of the compound propylene existing in the two forms:



I II

Here resonance does not take place, for to shift from form I to form II a hydrogen atom must be shifted from the first to the third carbon atom. The hydrogen atom is heavy and has too much momentum to be constantly shifting. Resonance is an electronic phenomenon.

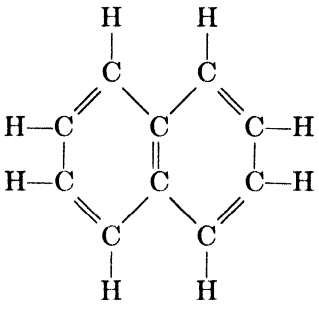
Resonance may take place between more than two bonds simultaneously. An example of this multiple resonance is the benzene molecule. Its structure is given by the two forms:



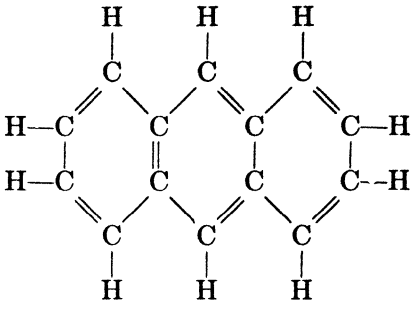
I II

The two forms are alike (contrast with the CO_2 molecule in which only two of the three forms are alike); no additional energy is needed to "lift" one form into the other. Resonance of this kind adds to the stability of the molecule as a whole. The bonds are not so easily broken. The breaking of the bond is usually necessary to bring about chemical change.

Many other molecules have increased stability, due to resonance. The following are good examples:



Naphthalene



Anthracene

In both of the above cases only one of the resonating forms is given.

The Structure of Graphite. Carbon exists in three forms; (a) amorphous carbon, (b) graphite, and (c) diamond. Amorphous carbon is that form which appears as lampblack and completely carbonized organic compounds such as sugar and coal. In this form the carbon does not have a well-defined crystal structure.

Graphite has a layer-like structure. Each layer has the structure indicated in Figure 3.10.

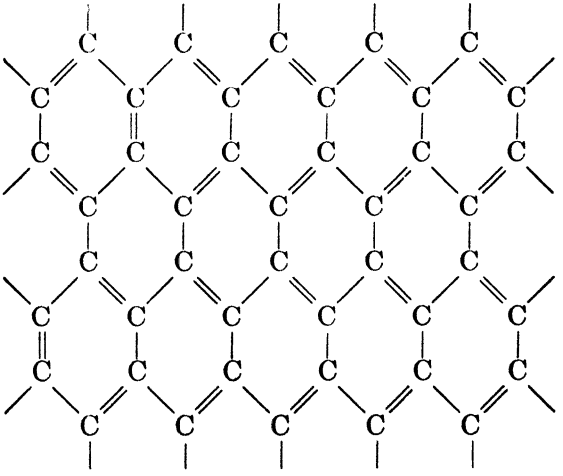


FIG. 3.10. The electronic structure of one layer of graphite.

It is easy to see that the double bonds can occupy positions other than those indicated in Figure 3.10. This is a resonating and hence a stable structure.

The greatest stability is obtained when the bonds are *conjugated*, i.e., when every other bond is a double bond. Note that this condition prevails for graphite, anthracene, naphthalene, and benzene. Note also in Figure 3.10 that each carbon atom has four bonds attached to it, i.e., each carbon atom has a rare gas structure. There are, therefore, no bonds or bonding electrons left over to connect the various layers of graphite. The layers are held together, not by covalent electrons nor by ionic attraction (there are no ions as in NaCl) but rather by van der Waals forces. These forces, which are to be discussed in a following section, are very weak as compared with the forces between the carbon atoms in each plane. The measured distances between the carbon atoms in each plane is 1.42 Å, while that between the carbon atoms in adjacent layers is 3.40 Å. The layers are about $2\frac{1}{2}$ times farther apart than are the carbon atoms in the same plane. Since the forces holding together the planes are very weak, graphite easily cleaves in this direction. As we should expect, graphite is flaky.

The Structure of Diamond. Diamond does not possess the hexagonal resonating structure of graphite but rather a tetragonal structure. In diamond each carbon atom is surrounded in space (not in a plane) by four other carbon atoms. The distances between all carbon atoms is the same. One can get a picture of this structure by imagining a single carbon atom with four bonds (lines) about it; the angles between all the lines are the same. Thus all the carbon atoms are tied to each other by shared electrons; i.e., covalent bonds. The whole diamond crystal is therefore one large covalently bonded molecule. The bonding forces between the carbon atoms is very great. This accounts for the hardness and the high melting point of diamond.

Induced Dipole Moments and van der Waals Forces. In Chapter 1 we discussed polar molecules and showed that molecules having unsymmetrical charge distributions were

subject to a turning or rotational effects in electrical fields. This turning effect is reflected in a large dielectric constant. The water molecule is of this kind. It has a large dielectric constant; it is polar and is said to have a large dipole moment (the average distance between the charge centers is relatively large).

Let us now consider the neon atom and its behavior between two condenser plates as shown in Figure 3.11. The neon atom consists of a small nucleus with a +10 charge surrounded by two shells of electrons — the inner shell consisting of two and

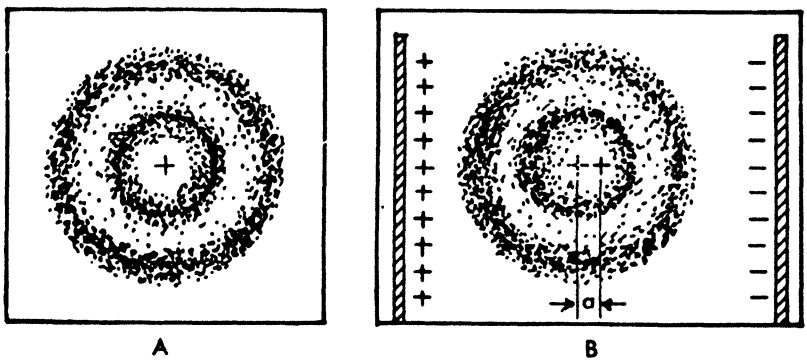


FIG. 3.11

A. The symmetrical neon atom. Shaded portion represents electron density.

B. The neon atom in an electrical field.

the outer shell of eight electrons. It is completely symmetrical and is therefore not a polar molecule. Yet some polarity can be induced into it, by its mere presence in an electric field.

Consider first Figure 3.11A. This shows the symmetry of the molecule — no dipole moment. By comparing this with Figure 3.11B we see that the position of the electronic shells has been slightly displaced by a very small amount (a) with respect to the nucleus. This small displacement gives rise to an *induced dipole moment* — a moment induced or brought about by the electric field. It is for this reason that non-polar substances have definite but small dielectric constants.

Similar considerations provide us a means for understanding

the van der Waals forces. Let us consider two neon atoms such as shown in Figure 3.11A, side by side, and close together. As we have said, the outer electrons do not completely screen and neutralize the nucleus. At short distances the nucleus of one atom is attracted by the negatively charged shells of the other while the two negative shells tend to repel each other. At some distances there is a net attraction. These combined attractive and repulsive forces are known as *van der Waals* forces. It is these forces that cause non-polar molecules to condense and form a liquid when the velocities of the gas molecules get slow enough to allow the forces to operate. It is also these forces that bind together molecules of a non-polar, non-ionic, or non-coordinately bonded solid.

For many kinds of molecules the van der Waals forces are solely responsible for the attraction between these molecules in the liquid state. Ordinary gasoline, although not a pure liquid, is an example of a substance with this type of molecular liquid binding.

It is these same forces that bind together the layers of carbon atoms in graphite.

The Different Kinds of Inter-atomic and Inter-molecular Binding Forces — A Recapitulation. In general there are two distinctly different kinds of forces that bind atoms and molecules to each other. One is the covalent bond (the sharing of electrons) and the other arises from electrostatic attraction between the charged particles that constitute the atom. The covalent binding asserts itself within the molecule. It is the force which is exerted by the coupling of electrons between two or more atoms and constitutes the chemical covalent bond.

The attractive forces due to electrostatic attraction may be divided into three kinds: (1) ionic attractive forces, as exemplified in the sodium chloride crystal; (2) dipole attractive forces, as exist between water molecules in ice; and (3) van der Waals forces, which exist between molecules having no dipole moments, i.e., between non-polar molecules.

Combinations of these various kinds of forces exist in many

solids and liquids. In diamond the atoms are held together purely by covalent forces. In graphite the forces are covalent in each layer and van der Waals between layers.

In sodium chloride the forces binding the Na^+ and Cl^- ions together are ionic, but in some crystals, particularly oxides, the attractive forces are partially ionic and partially covalent.

In water solutions of electrolytes — a water solution of NaCl, for example — the ions are hydrated due to the attractive forces between the ions and the polar molecules.

In a molecule such as butyl alcohol $CH_3(CH_2)_2\,CH_2OH$, one end of the molecule is polar. This polar end induces a charge shift in the whole molecule and so the attractive forces that hold these molecules together in both the liquid and solid state are both polar and van der Waals forces. The contribution of polarization to the binding force is illustrated in Table 9, in which the boiling points of various hydrocarbons are compared with their respective alcohols. The alcohol differs from the hydrocarbon in that a hydrogen atom at the end of the carbon chain is substituted by a polar OH group.

As would be expected, the difference between the boiling points, a measure of the difference between the binding forces,

TABLE 9

THE RELATIVE EFFECT OF A POLARIZING GROUP ON THE BOILING POINT

Compound	Formula	Boiling Point (° C)	Difference
Ethane	CH_3CH_3	−88.6	167.0
Ethyl Alcohol	CH_3CH_2OH	78.4	
Butane	$CH_3(CH_2)_2CH_3$	−.5	118.5
Butyl Alcohol	$CH_3(CH_2)_2CH_2OH$	118.	
Octane	$CH_3(CH_2)_6CH_3$	125.7	68.5
Octyl Alcohol	$CH_3(CH_2)_6CH_2OH$	194.5	
Dodecane	$CH_3(CH_2)_{10}CH_3$	214.5	40.5
Dodecyl Alcohol	$CH_3(CH_2)_{10}CH_2OH$	255.	

becomes less and less marked as the molecules get larger and the polar OH group has a smaller proportionate effect.

Ionic, Covalent, and Metallic Radii. We have discussed the force concepts which give rise to the different kinds of bindings, but there is another important factor that influences the binding and thereby influences the properties of the different chemical compounds. It is the sizes of the various atoms and ions in the crystalline state. These data are given in Table 10. The effect of ionic or atomic size on the chemical properties of a compound will be discussed throughout this text as we proceed.

TABLE 10

IONIC RADII (ACCORDING TO ZACHARIASEN) — BASED ON CRYSTAL COORDINATION NUMBER SIX

Valence	Ionic Radii in Ångstrom Units									
−2			O	1.45	S	1.90	Se	2.01	Te	2.23	Po	2.32
−1			F	1.33	Cl	1.81	Br	1.95	I	2.20	At	2.29
+1	Li	0.68	Na	0.98	K	1.33	Rb	1.48	Cs	1.67	Fr	1.75
+2	Be	0.30	Mg	0.65	Ca	0.95	Sr	1.12	Ba	1.28	Ra	1.35
+3	B	0.18	Al	0.45	Sc	0.68	Y	0.88	La	1.04	Ac	1.11
+4			Si	0.35	Ti	0.55	Zr	0.74	Ce	0.92	Th	0.99
+5							Nb	0.67			Pa	0.89
+6											U	0.83

The ionic radii, as exemplified in sodium chloride, differ considerably from the atomic radii of the covalent type, as in diamond. The values of the radii of the atoms in metals (the metallic radii) fall between those for the ionic and the covalent types. Furthermore, the radius of any ion depends both upon its charge and its crystal coordination number. For this course, therefore, the above table should be regarded as an approximation. In qualitative analysis, we deal largely with ionic crystals. We are, therefore, not so concerned with the atomic and metallic radii as we are with the ionic.

Questions and Problems

1. To what inert gas structure, if any, are the structures of the following atoms related:

(a) Ba	(f) Ni
(b) I	(g) Zn
(c) As	(h) Te
(d) H	(i) Al
(e) O	(j) Pd

2. Explain the fact that HCl in the pure liquefied form is not a good conductor of electricity while in aqueous solution it is.
3. Write the electronic structures (outer shells only) for the following:

(a) SO_4^{--}	(f) Br_2
(b) $CHCl_3$	(g) S^{--}
(c) PO_4^{---}	(h) KCl
(d) NH_4^+	(i) Na_2O
(e) CH_3CH_3	(j) NH_3

4. The uncharged radical NH_4 has been produced by the electrolysis of an aqueous solution of an ammonium salt, using mercury electrodes. From a consideration of the electronic structure of this radical, would you expect it to have properties similar to those of the gas CH_4 or to those of Na?
5. Make a table similar to Table 8 for the elements of the second sub-group (Zn, etc.). List three properties of the elements of this group that differ from those of the corresponding main group.
6. A molecule which has an odd number of electrons in its structure must have at least one unpaired electron. This unpaired electron gives rise to paramagnetic properties; i.e., the molecule is attracted into a magnetic field — it is a small magnet. NO, NO_2, and ClO_2 are paramagnetic, while N_2O and N_2O_4, and Cl_2O are not. Reconcile these facts with the above odd-electron rule of magnetic properties.
7. From the standpoint of electronic structure, explain (a) why graphite is flaky and (b) why diamond is very hard.
8. What is the general nature of van der Waals forces between molecules?
9. Why does ethyl alcohol, CH_3CH_2OH, have a much higher boiling

point than propane, $CH_3CH_2CH_3$, although both have about the same molecular weights?

10. Suppose that pure water lies between two plates of a condenser (as shown in Figure 1.5). The capacity of the condenser (the charge that the plates can carry) is increased by the presence of the polar water molecules. If the charge on the two plates is reversed, what will happen to the water molecules? Suppose now that the charge on the two plates is alternated more and more rapidly. Bearing in mind that the momentum of the water molecule must be overcome at each alternation, explain why the capacity of the condenser (the ability of the plates to carry a larger charge) will decrease when the frequency of alternation becomes very high. Liquid neon, in between the plates, would not show this effect. Why? (Hint: electrons are light and therefore have little momentum.)

11. What are the four kinds of forces that bind atoms and molecules together in the crystalline state?

CHAPTER

4

Quantized Atoms and Molecules

The Quantum Theory. After the development of the electric lamp, and particularly the carbon arc lamp, which once lighted the streets of our large cities, it became increasingly difficult to measure the intensity, i.e., to determine the candle power, of such lights by comparing them with the light of a candle made to given specifications, as had been done with previous light sources. Not only was the light emitted by these new sources much more intense than that emitted by the candle, but it also was different in color.

To better understand the nature of light emitters such as filaments and carbon arcs, and particularly how the character or the color of the light varied with the temperature of its source, the German bureau of standards, the *Reichsanstalt*, devised a light emitter which was called a *hohlraum*, i.e., a hollow. The *hohlraum* is merely a hollow object such as a sphere. When heated in a furnace the radiation within the hollow comes to temperature equilibrium with the walls of the hollow. There is a small hole in the wall of the hollow, and through this hole a small fraction of the light escapes for measurement. It was shown that the nature of the light emitted by a hollow is always the same, at a given temperature, regardless of the nature of the walls — the nature of the light is the same with copper, nickel, or black carbon walls. The light emitted from such a hollow, which is always at temperature equilibrium, is known as *black body* radiation.

White light is a composite of many colors. More specifically, since different kinds or colors of light are characterized by different frequencies (or wave lengths), white light is a composite of light of a wide range of frequencies. So also the light from a hollow, i.e., black body radiation — which at high temperatures appears to be white, at low temperatures red — is a composite of light of many frequencies.

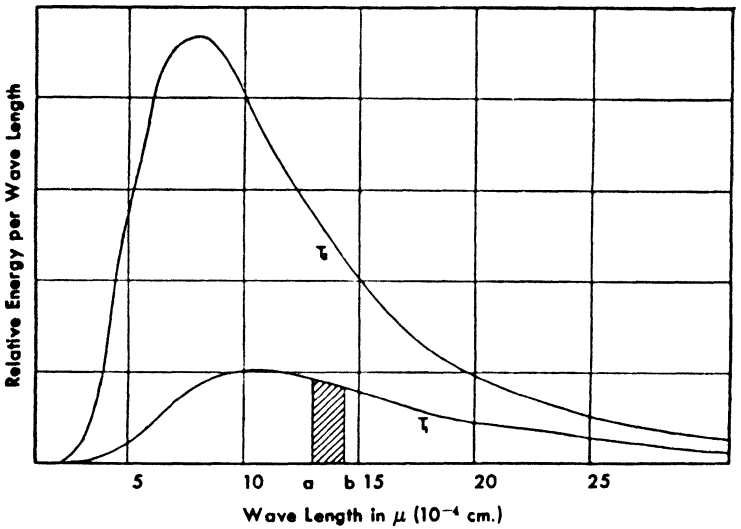


FIG. 4.1 Energy distribution of black body radiation.
$T_1 = 0°$ C, $T_2 = 100°$ C.

The light emitted from the hollow was analyzed. For example, experiments were made to determine what fraction of the total light energy lay between wave length 1.0μ and 1.1μ, what fraction between 1.1μ and 1.2μ, etc. ($1\mu = 1 \times 10^{-4}$ cm.). In such a way an intensity distribution was determined. It was found that this distribution of energy was different for different temperatures of the emitting black body. The distributions for two different temperatures are given in Figure 4.1.

To illustrate the interpretation of these curves, we pose the following question: What fraction of all the light emitted by a black body lies between the wave lengths a and b at tempera-

ture T_1? Draw vertical lines at a and b which meet the curve of T_1. The fraction of light emitted from these wave lengths is the ratio of the area contained by the curve between these two vertical lines (shaded area on the plot) to the total area under the curve for T_1. (To determine these areas one can use graph paper and count or estimate the number of squares in each area.)

It will be noted that at the higher temperature the maximum of the curve shifts toward shorter wave lengths, i.e., toward the blue. A greater proportion of blue light is given out at high temperatures than at low temperatures. Hence, a piece of iron heated to 700° C appears red, that at 1,000° C, white (the light emitted at 1,000° C contains more blue light) — one is red-hot, the other is white-hot.

The distribution of radiant energy in a hollow or black body as given in Figure 4.1 greatly interested scientists during the last 20 years of the last century.

By making various assumptions, they tried to calculate the shape of the curve in Figure 4.1. One assumption led to a reproduction of the left-hand side of the curve, and another assumption, to the right-hand side but no single assumption or hypothesis gave a reproduction of the complete curve with its maximum.

It was not until 1901 that Max Planck, a famous German physicist, hit upon the right solution and calculated the energy-distribution law and reproduced by calculation the curve given in Figure 4.1. But he could not do so without making a very radical assumption; namely, that light was emitted and absorbed in chunks, i.e., in *quanta*. This was the beginning of the quantum theory.

The assumption of Planck changed our picture of radiation. Light of a given frequency coming to us from the sun, for example, does not come as a continuous wave as shown in Figure 4.2A but rather in bursts or quanta as illustrated schematically in Figure 4.2B.

Radiation is measured by its absorption on a black surface which thereby raises the temperature of the absorbing surface.

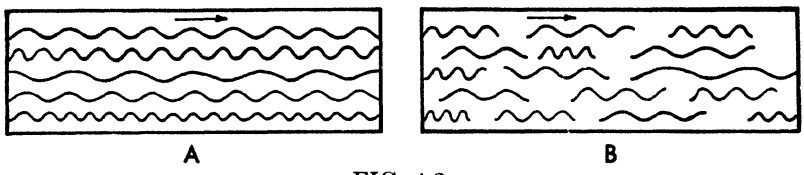


FIG. 4.2

A. Concept of continuous radiation. B. Concept of quantized radiation.

This energy is usually measured in *ergs*, the smallest fundamental unit of energy.

Planck found that to specify the amount of energy in ergs of each quantum of light, it was necessary to multiply the frequency (vibrations per second) of the light by a certain number which is known as Planck's Constant. In the shorthand of science he designated this multiplication factor (or conversion factor) as h. In this discussion we cannot go into the method by which the constant h was evaluated, lest we digress too far from our subject. The energy of each quantum (or burst of energy) is therefore equal to $h \times \nu$ or $h\nu$ (ν is the symbol for frequency, in vibrations per second). It should be noted that the amount of energy in one quantum of X-radiation (X-rays) with very high frequencies is much greater than in one quantum of red light of relatively low frequency.

Only a very few people became excited about the quantum theory in the early part of the present century, because it seemed possible that some other assumption might answer the question just as satisfactorily and there was no proof or positive sustaining experimental evidence to support Planck's hypothesis.

This condition of doubt existed for several years. Then came the *experimental* support of the quantum theory.

The Photoelectric Effect. In 1905 Einstein predicted, on the basis of the quantum theory, that when light is absorbed by a suitably sensitive metal surface and electrons are thereby emitted — as in our present photocells — one absorbed quantum of light should knock out only one electron from the surface. Also, he predicted that a quantum of high energy (light of high frequency) should knock out the electron at a higher

speed (i.e., higher kinetic energy) than would a low energy quantum. Robert A. Millikan, then of the University of Chicago, quantitatively verified Einstein's predictions. This was evidence substantiating the quantum theory.

The Photochemical Equivalence Law. At about the same time that Einstein predicted the effect of light on the ejection of electrons from a metallic surface, he also predicted another effect as the consequence of Planck's quantum theory. This effect had to do with the quantitative effect of light in photochemical experiments.

It is well known that light brings about chemical reactions. The photographic plate or film is an example. The outstanding example is the action of light on the green chlorophyll of plants which, by the fixation and reduction of the carbon dioxide in the atmosphere, results in the formation of starch, cellulose, and a host of other substances.

Einstein reasoned that, if light consists of quanta, i.e., chunks of energy, then in the simplest case one quantum of light energy should affect only one molecule. But, inasmuch as a molecule may not be able to decompose without reacting with another of its kind, i.e., one of its immediate neighbors, then two or even more molecules may change chemically for each quantum absorbed. The net result of Einstein's reasoning was that in the simplest photochemical experiment a simple and low multiple number of molecules should react for each quantum of light absorbed.

It so happened that one of the best possible experiments to prove the Einstein hypothesis was first tried for this purpose. This experiment was carried out by Emil Warburg, a German physical chemist. He used for his experiment the reaction involving the decomposition of hydrogen iodide, HI, by light. Warburg found that, for every quantum of light absorbed, two molecules of HI were decomposed into H_2 and I_2. Warburg's experimental results are given in Table 11.

These experiments are quite difficult to carry out. Deviations of the values from 2.00 undoubtedly represent experimental error.

TABLE 11

The Photochemical Decomposition of Hydrogen Iodide	
Wave Length Employed (Å units)	Molecules Decomposed Per Quantum Absorbed (Mean Values)
2,070	1.97
2,536	2.08
2,820	2.11

The mechanism later worked out and accepted for this reaction is as follows:

$$HI + h\nu \text{ (1 quantum of light)} = H + I \qquad (1)$$

In the first step the HI is decomposed into its atoms. The hydrogen atom produced by reaction (1) reacts with another HI molecule to make H_2 and another I atom.

$$H + HI = H_2 + I \qquad (2)$$

The HI molecule is sufficiently stable so that the iodine atoms formed in the reaction cannot react with it. That is, $I + HI = H + I_2$ is not possible because iodine atoms have a greater tendency to hold onto H atoms than onto other atoms of its own kind. In other words, an I atom holds an H atom tighter than it does another I atom.

Since the I atoms cannot react with HI molecules, they can react only with H atoms or with other I atoms. But there are very few H atoms present, because the H atoms are removed by the many HI molecules in the reaction mixture. For the same reason, it is very improbable that the H atoms recombine with each other to produce H_2. Accordingly, the I atoms react with each other to form I_2.

$$2I = I_2 \qquad (3)$$

We then summarize the various steps in the process:

$$HI + h\nu = H + I \quad (1)$$
$$H + HI = H_2 + I \quad (2)$$
$$I + HI = I_2 + H \text{ (energetically impossible)} \quad (x)$$
$$2H = H_2 \text{ (highly improbable)} \quad (y)$$
$$2I = I_2 \quad (3)$$

$$2HI + h\nu = I_2 + H_2 \quad (4)$$

Adding equations (1), (2), and (3) algebraically, neglecting (x) and (y), and cancelling like entities from opposite sides of the equations the resultant equation is (4).

According to equation (4), two molecules of HI are decomposed for every quantum ($h\nu$) absorbed. This is what Warburg found experimentally. If the HI molecules were decomposed proportionately to the total amount of energy (in calories or ergs) absorbed, rather than to the number of quanta (irrespective of calories or ergs) absorbed, then light of higher frequency (shorter wave length and greater energy) should have decomposed a proportionately larger amount of HI. This is not the case. Thus, Warburg again verified Planck's quantum theory.

It was fortunate that Warburg chose the right experiment to prove his point. Any other experiment might have given ambiguous results. It was later found that the reactions which give an unambiguous answer to this question are rare. In most photochemical reactions, much of the light energy absorbed is wasted by the heating of the mixture and only a fraction of the quanta absorbed cause chemical reactions; or the light may start a chain reaction, i.e., one quantum may give rise to the decomposition of hundreds or thousands of molecules. For example, if one quantum could set off the explosion of a mass of sensitive high explosives, then many molecules would decompose per quantum absorbed.

Fortunately, a well selected photochemical experiment by Warburg gave Planck's hypothesis an additional impetus.

However, thousands of later experiments proved the validity of the quantum theory. The explanation of the spectrum of atomic hydrogen by Niels Bohr gave rise to most of them.

The Emission of Light by Atoms. When the light from an incandescent filament is observed through a spectroscope, one sees a continuous spectrum in which the colors gradually shade from red to yellow, green, blue, and to violet. The spectroscope spreads and separates the various frequencies. If, instead of an incandescent filament, a neon lamp is used as the light source, one sees, instead of the continuous spectrum, a series of distinct red and green lines. The continuous spectrum of the light filament is like that of a *black body* — all frequencies are present. The line spectrum obtained from the neon lamp is that emitted by the atoms of neon and is known as an atomic spectrum.

Like the neon atom, the hydrogen atom (not the hydrogen molecule) also emits a line spectrum. Such a spectrum is

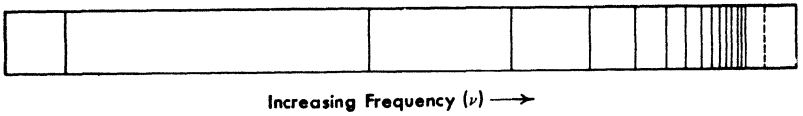


FIG. 4.3 The Balmer spectrum of the hydrogen atom.

emitted by some of the hot stars where the temperature is so high that hydrogen exists as atoms only. If one examines such a spectrum of hydrogen (Figure 4.3) it is apparent that some relatively simple regularity in the frequencies or wave lengths exists.

In the latter part of the last century Rydberg, a Swedish astronomer, found that the frequencies of the visible hydrogen lines could be expressed by the empirical (not theoretically derived) expression

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right),$$

in which ν is the frequency. R is a constant determined from the measurement of several lines, and n is a whole number having the value 3 or greater (each line in Figure 4.3 has a different value of n). The frequencies of the hydrogen lines fitted those calculated by this equation very exactly. The value of R (the Rydberg constant) was found to be 109,678.

The value of the constant is given here only to indicate how carefully the frequencies were measured and how accurately the Rydberg equation is known.

The spectra of other atoms were examined for similar correlations but no simple relationships could be found. For example, the spectrum of the sodium atom, using a sodium arc as the light source, was found to consist of not one series, as was the case with hydrogen, but four series; the ***sharp*** or *s* series, the ***principal*** or *p* series, the ***diffuse*** or *d* series, and the ***fundamental*** or *f* series. However, no one of these series showed any simple relationship between its various frequencies as did the hydrogen series.

The Bohr Theory. In 1913 it was generally accepted that the hydrogen atom consists of a proton nucleus with a charge of +1 and one outside electron with a charge of −1. Physicists tried to account for the hydrogen spectrum by calculation, using the known laws of electricity, magnetism, and mechanics. All failed except Bohr. He found the solution to the problem of the hydrogen spectrum by introducing a concept new in this field — the quantum theory. Bohr reasoned somewhat as follows. One hydrogen atom emits only one quantum at a time. The quanta emitted by hydrogen atoms have discreet i.e., very definite frequencies; hence, very definite energies. The atom, on emitting a definite amount of energy, $h\nu$, must also lose this same amount of energy. Therefore, the atom must be capable of possessing definite potential energy states. In other words, the internal energy of the hydrogen atom must itself be quantized. Either the atom does or does not possess this definite energy. There could be no way that the atom could possess internal energy between these definite states. It was a yes-no, all-or-nothing proposition. This is what we mean by quantization of energy in an atom or molecule. A whole number is assigned to represent the state of this quantized energy in its various forms. The internal energy of an atom or molecule must correspond to assigned quantum numbers — never to any intermediate values.

By using the classical laws of electrostatic attraction and

of centrifugal force (for the electron revolving around the nucleus), and by quantizing the angular momentum (related to energy), Bohr calculated the energies of the hydrogen atom in its various quantized orbits. Then, assuming that when light was emitted the electron in the energy state (or orbit) E_2 jumped to the energy state (or orbit) E_1 (never in between), and that the energy of the quantum was equal to the difference in energy of the two states E_2 and E_1,

$$E_2 - E_1 = h\nu$$

he was able to calculate the value for the Rydberg constant. His calculated value came within one part in 100,000 of the experimentally determined value. Furthermore, he calculated a radius for the hydrogen atom (the electron orbit) which was of the right order of magnitude. Such correlation between theory and experiment could hardly be fortuitous. This work of Bohr brought about the acceptance of the quantum theory and was the beginning of our present detailed knowledge of the quantized structure of atoms and molecules. It was in fact the beginning of modern physics and chemistry.

Originally, the various quantized orbits of the electron about the hydrogen nucleus were likened by many to the orbits of the planets about the sun, but now we think of these orbits as three-dimensional instead of planar orbits. We conceive them as shells.

According to the Bohr theory each shell (or orbit) is characterized by a principal quantum number, designated as n. The innermost orbit is characterized by $n = 1$, the next by $n = 2$, etc.

Light of definite frequency is emitted by the process of the electron leaving an outer shell and appearing in an inner one. The different possible transitions are illustrated in Figure 4.4.

The level, orbit, shell, or state, for which $n = 1$, is the only stable level for the hydrogen atom — that one in which the electron roams at ordinary temperatures. It is only when the hydrogen atom undergoes a severe collision with another atom as in a hot star, with a very fast electron as in an electric arc,

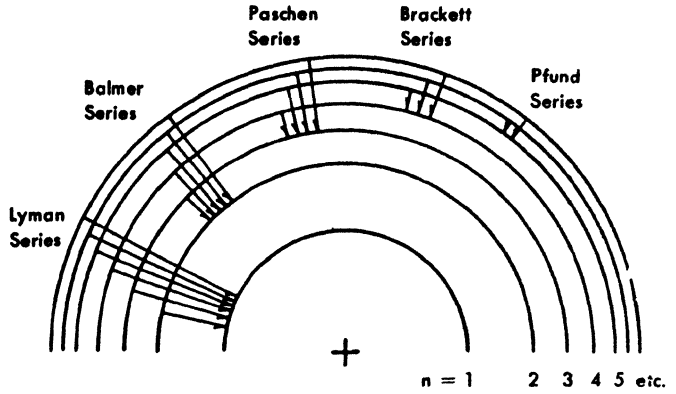


FIG. 4.4 Transitions involved in the lines of the different series of the hydrogen spectrum.

or even with a sufficiently high energy quantum, that its electron is knocked into one of the higher levels. When the hydrogen atom is in one of the higher shells or levels it is said to be *excited.* The orbit for which $n = 1$ is the only *real* one. The other orbits or shells are, in this case, known as *virtual* orbits or virtual shells. But these virtual shells are those which become real shells for atoms containing many electrons. Thus, the sodium atom has two electrons in the first or K shell for which the principal quantum number is 1; eight electrons in the second or L shell for which $n = 2$ (a *virtual* shell for the hydrogen atom), and one electron in the third or M shell for which $n = 3$ (also *virtual* in the case of the hydrogen atom). The single electron in the third or outermost shell of a sodium atom cannot have a principal quantum number less than 3 (since the two inner shells are filled), but it may have principal quantum numbers greater than 3 when it is in the excited state as in a Bunsen flame or a sodium lamp.

The Extension of the Bohr Theory. The simple theory of Bohr did not answer all the questions regarding the spectrum of hydrogen. When the apparently single lines of hydrogen are examined in a spectroscope of high resolving power it is found that each line is not a single line but consists of a

multiplet of several lines very close together. The problem then arose as to how to account for these multiple lines.

To explain these multiplets, it was assumed that the electronic orbits are not necessarily circular (i.e., the cross sections of the shells need not be circular). They could be in the form of ellipses. The Bohr theory was modified in such a manner that the momentum of the electron was quantized in two ways. One quantum number was assigned to represent the radial momentum (the momentum of increasing and decreasing the radius as it revolves in an ellipse) and the other, the angular momentum (related to the angular velocity). The principal quantum number, n, was the sum of these subsidiary quantum numbers. In the later development of the quantum theory that number which represented the angular part of the momentum was designated as l.

One of the quantum theory rules is that the quantum number l can have any value from zero to $n-1$. Thus, for the hydrogen atom in its lowest electronic state for which $n = 1$, l must be equal to zero. In the second state for which $n = 2$, the value of l can be either zero or one (minus values of l are excluded). The electrons for which $l = 0$ are called s electrons; for $l = 1$, p electrons; for $l = 2$, d electrons; and for $l = 3$, f electrons. The old notations used to describe the spectroscopic series for the sodium atom were taken over to describe the different kinds of quantized electrons — the symbols s, p, d, and f have only historic significance. The above rule is recapitulated in the following tabular form.

TABLE 12

Principal Quantum Number	Possible l Quantum Numbers and Corresponding Designations of Electrons			
n	s	p	d	f
1	0			
2	0	1		
3	0	1	2	
4	0	1	2	3

To fully explain the splitting of spectral lines (or levels) when an emitting atom is in a magnetic field, two other quantum numbers were introduced; the magnetic quantum number m, and the spin quantum number s.

The magnetic quantum number can have all values from $+l$ to 0 to $-l$ — another quantum theory rule. Thus if $l = 2$ (for a d electron) the magnetic quantum number can have values of +2, +1, 0, −1, −2.

The relationship between the quantum number l and quantum number m is as follows.

TABLE 13

Relationship between l and m

Values of l	Possible Values of m
0	0
1	+1, 0, −1
2	+2, +1, 0, −1, −2
3	+3, +2, +1, 0, −1, −2, −3

It will be observed that the total number of m values is equal to $2l + 1$.

The spin of the electron (another consideration) can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. The fraction $\frac{1}{2}$, rather than a whole number, is used to give a consistency to the whole quantized system. Further elaboration of the quantum numbers is beyond the scope of this elementary treatment. The positive and negative values for these quantum numbers indicates an orientation of the orbit or of the electron either *with* or *against* the magnetic field.

The quantum theory rules may seem to be in the form of arbitrary assumptions, invented to account for the known chemical facts. They were, in fact, derived mathematically from very general assumptions and, in most cases, to account for spectroscopic rather than chemical phenomena. Because of the mathematical complexities we are forced to omit the more fundamental derivations in this course. We must, for

the present, therefore, accept the above rules on a "rule-of-thumb" basis, recognizing, however, that they have firm foundation both in theory and in fact.

Before we can go any further in applying the quantum theory to the structure of atoms, we must consider one very fundamental rule, the Pauli Exclusion Principle. This principle states that in any given atom no two electrons can have identical quantum numbers — three of the four quantum numbers may be alike but the fourth must differ.

On the basis of the Pauli Exclusion Principle let us determine the maximum number of electrons that can exist in the second shell of an atom. For this shell $n = 2$. The quantum number l can then have values of 1 or 0. First consider the electrons for which $l = 0$ (s electrons); m also equals 0. But the spin number can be $+\frac{1}{2}$ and $-\frac{1}{2}$, so we find a maximum of 2 s electrons. Now consider how many electrons can have the value of $l = 1$ (p electrons). For this case $m = +1$, 0, and -1. Each electron which has a spin value of $+\frac{1}{2}$ can have 3 values of m, and each electron with a spin of $-\frac{1}{2}$ can also have 3 m values. The total number of p electrons is, therefore 6. We may recapitulate this in the following tabular form. In Table 14 all combinations of the quantum numbers are accounted for.

TABLE 14

Quantum Numbers	n	l	m	s	
	2	0	0	$+\frac{1}{2}$	2 s electrons
	2	0	0	$-\frac{1}{2}$	
	2	1	1	$+\frac{1}{2}$	
	2	1	1	$-\frac{1}{2}$	
	2	1	0	$+\frac{1}{2}$	6 p electrons
	2	1	0	$-\frac{1}{2}$	
	2	1	-1	$+\frac{1}{2}$	
	2	1	-1	$-\frac{1}{2}$	

In the same way it can be shown that the third shell can contain only 18 electrons as a maximum. This shell, for which

$n = 3$, contains all of the electrons described in Table 14 (total of 8) plus 10 d electrons, with $l = 2$, and $m = +2, +1, 0, -1,$ and -2.

Table 15, on the next page, gives the electronic configurations of all the elements.

To the student reading these rules for the first time, they must seem very confusing. However, to relieve this confusion, let us review the quantum rules.

(1) When the electron is in its innermost shell, $n = 1$; in the second shell, $n = 2$; etc.

(2) l can have any value between zero and $n - 1$. (Negative values are not allowed.)

(3) m, the magnetic or the 3-dimensional number, can have values ranging from $+l \rightarrow 0 \rightarrow -l$.

(4) s, the spin number, can have values of either $+\frac{1}{2}$ or $-\frac{1}{2}$.

(5) No two electrons in an atom can have all of the above four quantum numbers alike.

Now, read the last several pages again and check the statements in these pages with this summary.

Henceforth in this text we shall not refer to the subsidiary quantum numbers to designate electrons in the atom. For the purposes of chemistry we need use only the principal quantum number and the kind of orbit, s, p, d, f, etc., to describe the electron. Thus an electron designated as 3 d is in the third shell ($n = 3$) and it occupies a d orbit ($l = 2$).

Instead of using the term *electron orbits* we now designate the characteristics of an electron in an atom by the term *orbital*. The orbital is not to be regarded as a definite path but rather as a term which describes the probability as to where or in what direction in space the electron spends its time. The geometrical concept of the orbital is that of a shell of a given thickness in which the electron travels. It spends most of its time in the center portion of this shell layer.

The orbital may be likened to an eggshell, with the difference that the shell does not have a constant density. Going from the outside to the inside of the shell-layer the density is at first very low (zero), then increases toward the center, and

TABLE 15

ELECTRON CONFIGURATIONS OF THE ELEMENTS *

		K	*L*		*M*			*N*				*O*				*P*			*Q*
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	Neon		6	2	3													
S	16	core		6	2	4													
Cl	17	2	2	6	2	5													
A	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	Argon	6	2	6	3	2											
Cr	24	2	core	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb	41	2	2	6	2	6	10	2	6	4		1							
Mo	42	2	2	Krypton	6	10		2	6	5		1							
Tc	43	2	2	core	2	6	10	2	6	6		1							
Ru	44	2	2	6	2	6	10	2	6	7		1							
Rh	45	2	2	6	2	6	10	2	6	8		1							
Pd	46	2	2	6	2	6	10	2	6	10									

* The electronic assignments for elements 89 to 98 are very tentative.

		K	*L*		*M*			*N*				*O*				*P*			*Q*
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
Ag	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						
Xe	54	2	2	6	2	6	10	2	6	10		2	6						
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba	56	2	2	6	2	Xenon core		6	10			2	6			2			
La	57	2	2	6	2	6	10	2	6	10		2	6	1		2			
Ce	58	2	2	6	2	6	19	2	6	10	1	2	6	1		2			
Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1		2			
Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1		2			
Pm	61	2	2	6	2	6	10	2	6	10	4	2	6	1		2			
Sa	62	2	2	6	2	6	10	2	6	10	5	2	6	1		2			
Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1		2			
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1		2			
Ds	66	2	2	6	2	6	10	2	6	10	9	2	6	1		2			
Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1		2			
Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1		2			
Tu	69	2	2	6	2	6	10	2	6	10	12	2	6	1		2			
Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1		2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
Fr	87	2	2	6	2	6	10	2	Radon core			2	6	10		2	6		1
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10	1	2	6	1	2
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	1	2

then drops off again to zero on the inside. The electron spends its greatest amount of time where the density is greatest. Thus, we do not picture the neon atom as that given in Figure 4.5 but rather as that given previously in Figure 3.11A.

Directions of Atomic Orbitals. There is only one kind of s orbital (since $l = 0$ and $m = 0$). One pair of s electrons occupies an orbital which is a spherical shell about the nucleus. However, there are *three* sets of p orbitals ($m = +1, 0, -1$). Calculations indicate that the axes of these orbitals (with the nucleus at the crossing point) are at *right angles* to each other. The three types of p orbitals are therefore sometimes designated as p_x, p_y, and p_z. As would be expected from the magnetic quantum numbers ($+2, +1, 0, -1, -2$) there are 5 kinds of d orbitals. These have been calculated to lie along the edges of a 5-sided pyramid.

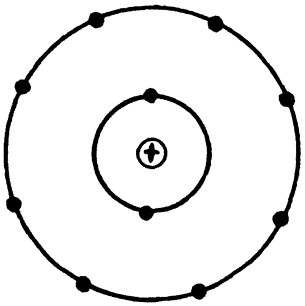


FIG. 4.5 The obsolete concept of the neon atom (*see* Fig. 3.11A)

The directions of the different kinds of orbitals determine to a large extent the directions of the chemical bonds. When the electrons of one atom are paired with the electrons of other atoms, the positions of the atoms with respect to each other are heavily influenced by the orbital directions of the component atoms.

The Combination of Orbitals to Form Electron Pairs. While Table 15 indicates the number of different kinds of orbitals in each shell, it does not indicate which of these are unpaired. As the result of spectroscopic investigations, the number of such unpaired electrons can be determined. For example, Table 15 indicates for the carbon atom two $1s$ electrons, two $2s$ electrons, and two $2p$ electrons. Actually the $2p$ electrons are unpaired. We may then designate this structure in more detail by $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$ — *the superscripts in this description indicate the number of electrons of that particular kind.*

There is a general principle (another quantum rule) which states that electrons in any given shell do not pair (to neutralize their spins) until they are forced to by the Pauli Exclusion Principle. For example, the detailed structure of the nitrogen atom is $1s^2\ 2s^2\ 2p_x\ 2p_y^1\ 2p_z^1$ and for oxygen $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$.* (The superscripts indicate the number of electrons in that particular state — thus $2s^2$ indicates two $2s$ electrons.) There are only 3 magnetic quantum numbers available for a p orbital (+ 1, 0, − 1) so the fourth p electron in oxygen must pair with another; hence two $2p_x$ electrons.

The two unpaired p electrons in oxygen will couple or pair with an unpaired electron of another atom — *the valence of oxygen is two.*

When the oxygen atom forms water with two hydrogen atoms, the two unpaired p electrons of the oxygen atoms pair with the single s electrons of the hydrogen atoms. Since the p orbitals are at *right angles* to each other we might expect the bond angles in water to be 90° apart. Actually the bond angle in water is 105°.

This difference between the measured 105° and the expected 90° is due to the electrostatic repulsion of the two hydrogen atoms for each other. We have previously indicated that the H_2O molecule is polar. The hydrogen atoms are therefore not screened or neutralized completely and are positively charged. These positive charges repel each other and spread the bonding angle.

Likewise, we should expect the three bonding angles in NH_3 to be at *right angles* to each other but again the electrostatic repulsion spreads these angles to 108°. The bond angles of the NH_3 molecule therefore are in the shape of a tetrahedron or three-sided pyramid.

From the configuration of the carbon atom ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$) we might expect carbon to be bivalent with only the p electrons forming bonds. Such is the case with CO. However, the tetravalent character of carbon is explained by the fact that

* The superscript one (1) to represent one electron in a given state is usually omitted. Thus $2p_y^1$ is equivalent to $2p_y$.

the pairing of the s electrons becomes very much weakened after the p electrons have bonded (in the process of chemical reaction). The s electrons then on further reaction become unpaired and are *promoted* to bonding electrons. Resonance takes place between all of the electrons in the second shell, and all become identical. The carbon bonding axes are tetrahedral in shape. These bonds are hybrids between the $2s$ and $2p$ orbitals of the carbon atom, just as the mule is a hybrid between the horse and the donkey. All four bonds become alike — mules.

Quantized Vibration and Rotation. All molecules in the gaseous state undergo both vibration and rotation. The vibrational motion is along the axis between two atoms. Like the electronic energy this vibrational energy is quantized. When the vibrational energy becomes great enough the bond breaks and the molecule dissociates.

The rotational energy can be resolved about three axes. This energy is also quantized. Three axes require three quantum numbers.

The vibrational and rotational energies are small as compared with electronic energies and hence play no part in the determination of bonding and structure of molecules.

Questions

1. What is meant by *black body* radiation?
2. For what purpose was the quantum theory first proposed?
3. What predictions did Einstein make which, when verified by experiment, gave support to the quantum theory?
4. The equation representing the Lyman Series is

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where n is greater than 10K. That for the Balmer Series is

$$\nu = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$$

where n is greater than 2. What is the equation which represents the Paschen Series? (See Figure 4.4.)

5. Using the Pauli Exclusion Principle, satisfy yourself that the maximum number of electrons that can be in the N shell, for which $n = 4$, is 32.
6. How many unpaired electrons are there in (a) the silicon atom, (b) the phosphorous atom?
7. Why are the bonding angles between the H atoms in the water molecule 105° rather than the expected 90°?

CHAPTER

5

Oxidation and Reduction

All chemical reactions may be classified into two types: those which involve oxidation and reduction and those which do not. The reactions of the latter type consist of exchanges of atoms or groups of atoms without any change in the valence states of any of the reactants or, in terms of the electronic concept of matter, without any transfer of electrons. Familiar examples of reactions in water solution which do not involve any change in the valence state are:

$$Ag^+ + Cl^- = AgCl(\text{solid}) \quad (1)$$

$$Ba^{++} + SO_4^{--} = BaSO_4(\text{solid}) \quad (2)$$

$$SO_3^{--} + 2H^+ = SO_2 + H_2O \quad (3)$$

$$Cu^{++} + H_2S = CuS(\text{solid}) + 2H^+ \quad (4)$$

In each of these reactions the valence states of the atoms or groups comprising the products are the same as those of the reactants. The equations representing these reactions are relatively simple as compared with those of the oxidation-reduction type.

Since we shall encounter oxidation-reduction equations so often in our later work it is essential that we have a clear understanding of this type of reaction at the outset. We must be certain that we fully understand the balancing of oxidation-reduction equations to the extent that the balancing of any equation whatsoever will never baffle us. Once the principles of equation balancing are mastered there will never be any

need to remember any equation in all its details. We shall, also, in this chapter introduce the concept of ***valence number,*** sometimes known as ***oxidation number,*** a direct consequence of our previous discussion.

Balancing of Oxidation-Reduction Equations

To understand clearly oxidation-reduction processes it is essential to obtain a thorough working knowledge of a systematic scheme for balancing equations.

As an example of an oxidation-reduction reaction we shall choose the reaction of ferrous ion with chlorine in water solution.

$$2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^{-}* \qquad (5)$$

It is apparent that the condition of the iron and of the chlorine in the reactants is entirely different from that in the products. In the reactants the ferrous ion carries two positive charges while in the product the ferric ion bears three positive charges. Likewise, molecular chlorine is a reactant but the only product containing chlorine is the chloride ion. Both reactants have changed their valence states. In the course of the reaction the iron becomes more positive and the chlorine more negative. The valence number of the iron in equation (5) changes from +2 to +3, whereas that of the chlorine changes from 0 to −1. Thus, the ferrous ion loses one electron in the reaction while the chlorine atom gains one electron (the chlorine molecule accordingly gains two electrons). Substances which lose electrons are ***reducing agents,*** while those which gain electrons are known as ***oxidizing agents.*** *The oxidizing agent oxidizes the reducing agent and the reducing agent reduces the oxidizing agent.* In the reaction under discussion the ferrous ion is the reducing agent and it is oxidized to the ferric ion since it loses an electron. On the other hand, the chlorine in the zero state

* In writing equations for oxidation-reduction reactions we shall continue to omit those substances which do not contribute in any way to the progress of the reaction. For example, in equation (5), if a solution of ferrous sulfate were the reactant employed, we would omit the sulfate ion (SO_4^{--}) from both sides of the equation.

is the oxidizing agent and it is reduced to the chloride ion since it gains an electron. Every oxidation process is simultaneously accompanied by a reduction process; the two processes are associated with each other and cannot act independently. The total number of electrons gained by an oxidizing agent in a given reaction must equal the total number of electrons lost by the corresponding reducing agent. It is through this concept that we shall balance equations of the oxidation-reduction type.

The Valence Number. Before we balance equation (5) on the basis indicated above let us consider parenthetically what is meant by a change in valence state or valence number. In some cases the valence number of an atom in a molecule is equal to the charge that the atom will acquire when the molecule dissociates in water to produce ions. Thus, the valence number of iron in ferrous chloride is +2, the same as the charge on the ferrous ion (Fe^{++}) in solution. In other cases, however, the valence number of an atom in a molecule is assigned in a more arbitrary manner; its value does not correspond to the charge on any known ion of that element. The valence number of carbon in methane (CH_4) is −4. A carbon ion with four negative charges is not known. In assigning a valence of −4 to carbon in methane, we have quite arbitrarily assumed a valence number of +1 for hydrogen. Acids dissociate to give the hydrogen ion, H^+, which bears a +1 charge. Likewise, water to a smaller extent dissociates to give hydrogen ions as one of the products. Methane, to the best of our knowledge, does not dissociate in solution to give hydrogen ions, yet in considering the valence number of the molecule we recall the concept that hydrogen atoms have a tendency to lose one electron and produce hydrogen ions. To be consistent we therefore assign a +1 valence number to hydrogen in methane. In fact, in all compounds containing hydrogen this same valence number for the hydrogen atom is arbitrarily assumed and the valence numbers of other atoms are assigned accordingly.*

* An exception to this statement is found in the case of the hydrogen compounds (hydrides) of the strongly electropositive elements such as LiH, NaH, CaH_2, etc. In these compounds the valence number is evidently −1.

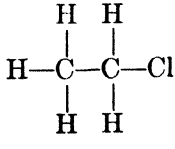
The valence number of the oxygen atom in the water molecule is −2 and since the state of oxidation of the oxygen atom in water is the same as it is in oxides, it is assumed that the valence number of oxygen in all oxygen compounds, with the exception of the peroxides, is −2. In hydrogen peroxide, as well as in all peroxides, each oxygen atom must have a valence number of −1 if the valence number of each hydrogen atom is to be retained as +1.

In assigning the valence number of any atom, the only principle to be observed is that the algebraic sum of the valence numbers of all atoms in the molecule under consideration must equal zero in the case of neutral molecules, or must have the same value as the charge in the case of an ion. The following examples will serve to illustrate this point.

Substance	*Atoms*	*Valence Number per Atom*	*Total Charge*
Water	2 hydrogen	+1	+2
	1 oxygen	−2	−2
			Net charge 0
Sulfuric Acid	2 hydrogen	+1	+2
	4 oxygen	−2	−8
	1 sulfur	+6	+6
			Net charge 0
Ammonium ion	4 hydrogen	+1	+4
(NH_4^+)	1 nitrogen	−3	−3
			Net charge +1

In the last case the net charge of +1 is the same as the charge on the ion.

In some cases there may be two atoms of the same element but in different valence states in one and the same molecule. For the purpose of balancing equations, either the algebraic sum or the average valence number is used. For example, consider the valence state of carbon in ethyl chloride,



From the structural formula it is apparent that one carbon atom has a valence number of −3 and the other carbon atom a valence number of −1. The sum of the valence numbers of these two carbon atoms is −4. This result could also be determined from the empirical formula, C_2H_5Cl. The algebraic sum of the valence numbers of all the atoms must equal zero. Thus, five hydrogen atoms give +5; one chlorine atom, − 1; and the two carbon atoms must give −4 to give an algebraic sum equal to zero. Obviously the average valence number of the carbon atoms is −2 and for purposes of balancing equations this value should be used.

Atoms in the elementary state have a valence number of zero. Thus elementary copper, zinc, sodium, chlorine, hydrogen, oxygen, etc., possess atoms which as such function in reactions with a valence number of zero. In order that an atom have a positive or a negative valence number the atom must be in the form of an ion or in molecular combination.

Returning to the example of the oxidation of ferrous ion by chlorine, we may balance the equation on the basis of an equality in the number of electrons lost and gained. Writing the unbalanced equation

$$Fe^{++} + Cl_2 = Fe^{+++} + Cl^- \qquad (6)$$

we see that when one ferrous ion changes to a ferric ion the process involves a loss of one electron, and when one chlorine atom in the zero valence state changes to a chloride ion, the process involves the gain of one electron. From an electronic standpoint the equation would be balanced if chlorine existed as a single atom and not as Cl_2, but since we know that elementary chlorine under ordinary conditions of temperature exists in the molecular form, as two atoms to the molecule, we must maintain it in this condition in our equation. The two chlorine atoms are held together in the molecule through a sharing of electrons, in other words, as a non-polar binding. This condition places each chlorine atom in the zero state of valence. Since two atoms of chlorine would necessarily gain a total of two electrons, and since one ferrous ion loses only one elec-

tron, equation (6) is not balanced. It may be balanced electronically, as illustrated in the following equation in which the change in valence numbers is indicated.

$$\underset{\text{2} \times 1\ e^- \text{ lost}}{\overset{+2}{Fe^{++}}} + \underset{\text{2 } e^- \text{ gained per molecule}}{\overset{0}{Cl_2}} = \overset{+3}{Fe^{+++}} + \overset{-1}{Cl^-} \qquad (7)$$

For an electronic balance the gain of two electrons by the two chlorine atoms of the chlorine molecule must be equaled by a loss of two electrons by the ferrous ion. The latter process requires two ferrous ions. In this particular case the complete balancing is relatively simple since no other substances are involved in the reaction aside from the oxidizing and reducing agents and their products. Thus, the completely balanced equation is

$$2Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^- \qquad (8)$$

In the following sections we shall present examples to illustrate the completion of more complicated equations after they have been balanced from the electronic standpoint only.

Oxidation and Reduction in Acid Solution. Many oxidation-reduction reactions take place with the production or consumption of hydrogen ions and these ions must therefore be included in the balanced equation. Among those substances which act as oxidizing agents in acid solution are included permanganate ion, MnO_4^-, dichromate ion, $Cr_2O_7^{--}$, and nitrate ion, NO_3^-. In the process of oxidation and reduction some or all of the oxygen atoms in these ions react with hydrogen ions to produce water. Thus chloride ion is oxidized by permanganate ion in acid solution to give the products shown in the following equation:

$$\overset{+7}{MnO_4^-} + \overset{-1}{Cl^-} + H^+ = \overset{+2}{Mn^{++}} + \overset{0}{Cl_2} + H_2O \qquad (9)$$

The procedure is, (1) assign valence numbers, (2) balance the equation electronically, and (3) make a complete balance. It is evident that the MnO_4^- ion is the oxidizing agent and

the Cl^- ion the reducing agent; the MnO_4^- ion is reduced and the Cl^- ion is oxidized. The valence number of the manganese atom in the MnO_4^- ion is +7, while in the Mn^{++} ion it is +2. Evidently a change has taken place which involves a gain of five electrons by the MnO_4^- ion since the valence number of the oxygen is not changed in this reaction. Chloride ion, valence number −1, changes to free chlorine of zero valence number, which process can be accounted for only by a loss of one electron per Cl^- ion. The change in the electrons may now be represented as

$$\underset{\text{5 } e^- \text{ gained}}{\overset{+7}{MnO_4^-}} + \underset{\text{1 } e^- \text{ lost}}{\overset{-1}{Cl^-}} + H^+ = \overset{+2}{Mn^{++}} + \overset{0}{Cl_2} + H_2O \qquad (10)$$

For an electronic balance the same number of electrons must be taken up by the oxidizing agent as is given up by the reducing agent. Therefore five Cl^- ions are required for each MnO_4^- ion to produce an exchange of five electrons, and therefore

$$MnO_4^- + 5Cl^- + ?H^+ = Mn^{++} + \tfrac{5}{2}Cl_2 + ?H_2O \qquad (11)$$

Multiplying both sides of the equation by 2 to remove the fraction $\frac{5}{2}$, the equation becomes

$$2MnO_4^- + 10Cl^- + ?H^+ = 2Mn^{++} + 5Cl_2 + ?H_2O \qquad (12)$$

A balance of the hydrogen and oxygen atoms is still lacking. However, it will be observed that all of the oxygen of the oxidizing agent through combination with hydrogen ions is converted into water. Since two molecules of permanganate ion contain eight oxygen atoms, eight molecules of water must be formed. In turn, eight molecules of water require sixteen hydrogen ions and the equation is finally written

$$2MnO_4^- + 10Cl^- + 16H^+ = 2Mn^{++} + 5Cl_2 + 8H_2O \qquad (13)$$

When the permanganate ion acts as an oxidizing agent in acid solution the manganese is always reduced to the manganous ion, Mn^{++}.

Another very satisfactory method for completing the balancing of the equation, after the oxidation-reduction part has been taken care of, is one involving a balance of the ion charges (not necessarily valence numbers) on both sides of the equation. Beginning with equation (12) the coefficients for the hydrogen ions and water molecules may be determined as follows: On the right side of the equation the only charged particles are the two Mn^{++} ions. The total ionic charge on the right is therefore +4. The algebraic sum of the charges on the left side must also be +4. Neglecting the H^+ ion for the moment, which is not balanced, the total charge on the left side is found to be −12, $(2MnO_4^- + 10Cl^-)$. Sixteen H^+ ions are necessary to make the algebraic sum +4, $(-2 - 10 + 16 = +4)$. The sixteen H^+ ions produce eight molecules of water. As a final check on the method the number of oxygen atoms on both sides of the equation must be the same, which is the case for the finally balanced equation (13). This method of final balance is often simpler than the alternative method previously given.

Another strong oxidizing ion in acid solution is the dichromate ion, $Cr_2O_7^{--}$, which in this medium is always reduced to the chromic ion, Cr^{+++}. Thus, iodide ion is oxidized by $Cr_2O_7^{--}$ to I_2:

$$\underset{\text{6 } e^- \text{ gained}}{\overset{2\times(+6)}{Cr_2O_7^{--}}} + \overset{-1}{I^-} + H^+ = \underset{\text{1 } e^- \text{ lost per atom}}{\overset{2\times(+3)}{2Cr^{+++}}} + \overset{0}{I_2} + H_2O \qquad (14)$$

The valence number of the chromium atom in the $Cr_2O_7^{--}$ ion is +6, but since there are two chromium atoms per ion the total charge is +12. When one $Cr_2O_7^{--}$ ion is reduced to two Cr^{+++} ions there is a gain of six electrons, three electrons for each chromium atom, whereas one I^- ion loses one electron in the oxidation to an iodine atom in the iodine molecule. For an electronic balance it is evident that six I^- ions are required

to take care of the gain of six electrons by the chromium atoms of the $Cr_2O_7^{--}$ ion; thus

$$Cr_2O_7^{--} + 6I^- + ?H^+ = 2Cr^{+++} + 3I_2 + ?H_2O \qquad (15)$$

The equation is now balanced electronically. Making the final balance by means of the ionic charge method we find a charge of +6 on the right side of the equation due to the two Cr^{+++} ions, and a charge of −8 on the left side ($Cr_2O_7^{--} + 6I^-$). To make the algebraic sum of the charges on the left equal that on the right, namely +6, it is necessary to add a charge of +14 to the left side. This is accomplished by using fourteen H^+ ions which form seven molecules of water. The final completely balanced equation is therefore

$$Cr_2O_7^{--} + 6I^- + 14H^+ = 2Cr^{+++} + 3I_2 + 7H_2O \qquad (16)$$

The correctness of the balance is checked by the presence of seven oxygen atoms on each side of the equation.

The alternative method of making the final balance (beginning with equation 15) is somewhat simpler. The seven oxygen atoms on the left are completely converted into water. It is evident that in order for this to take place fourteen H^+ ions must be furnished and seven molecules of water will be formed.

Oxidation-reduction equations can be balanced without the introduction of the concept of electron change. When this is done one merely takes into account the positive or negative change in valence number. For example, in equation (14) the valence number of the chromium atoms in the $Cr_2O_7^{--}$ ion changes from +12 to +6, a net change of −6, in the process of conversion to two Cr^{+++} ions. The valence number of each I^- ion changes from −1 to zero, a net change of +1, in going to free iodine. To make the net positive charge equal the net negative charge six I^- ions are necessary.

We shall now consider an example of the balancing of an oxidation-reduction equation in which the reducing agent contains more than one kind of atom undergoing change in valence

number. For this purpose let us choose the reaction of arsenous sulfide with nitric acid in which there is produced arsenic acid, free sulfur, and nitric oxide.

$$\begin{array}{lllllllll} 2\times(+3)+3\times(-2) & & +5 & & 2\times(+5) & 0 & +2 & & \\ As_2S_3 & + & NO_3^- + H^+ & = & 2HAsO_3 & + 3S & + NO & + & H_2O \\ \multicolumn{2}{l}{\text{10 } e^- \text{ lost}} & \multicolumn{3}{l}{(2\times2)+(3\times2)} & & & & \\ & & \multicolumn{3}{l}{3\ e^- \text{ gained}} & & & & \end{array} \qquad (17)$$

The valence number of the arsenic atom in As_2S_3 is +3 and the valence number of the sulfur in this molecule is −2. Both the arsenic and the sulfur change valence number and the total change for each As_2S_3 molecule is +10 as indicated in the above equation. On the other hand, each NO_3^- ion gains three electrons in its conversion to nitric oxide. Thus ten NO_3^- ions and three molecules of As_2S_3 are necessary to produce the same loss as gain in electrons (namely 30).

$$3As_2S_3 + 10NO_3^- + ?H^+ = 6HAsO_3 + 9S + 10NO + ?H_2O \quad (18)$$

Balancing equation (18) by the ion charge method, we find zero charge on the right side of the equation and a charge of −10 on the left (omitting the H^+ ion). Accordingly, ten H^+ ions are necessary to produce a net ionic charge on the left equal to zero. This amount of H^+ ion produces two molecules of water since six H^+ ions are required for the production of six molecules of $HAsO_3$ and the finally balanced equation becomes

$$3As_2S_3 + 10NO_3^- + 10H^+ = 6HAsO_3 + 9S + 10NO + 2H_2O \quad (19)$$

Checking the balancing by the oxygen atom count we find thirty oxygen atoms on each side of the equation.

Oxidation and Reduction in Alkaline Solution. As an example we shall choose the oxidation of chromite ion, CrO_2^-, by hypochlorite ion, ClO^-, in the presence of hydroxide ion, OH^-. The unbalanced equation with the valence numbers indicated is

$$\overset{+3}{CrO_2^-} + \overset{+1}{ClO^-} + OH^- = \overset{+6}{CrO_4^{--}} + \overset{-1}{Cl^-} + H_2O \quad (20)$$

$2\times3\ e^-$ lost; $3\times2\ e^-$ gained

and the electronic balance is

$$2CrO_2^- + 3ClO^- + ?OH^- = 2CrO_4^{--} + 3Cl^- + ?H_2O \quad (21)$$

Since the algebraic sum of the charges on the ions on the right side of the equation is -7 and that on the left (leaving the OH^- out of consideration for the present) is -5, it is evident that two OH^- ions are required on the left. One molecule of water is formed and the balanced equation is

$$2CrO_2^- + 3ClO^- + 2OH^- = 2CrO_4^{--} + 3Cl^- + H_2O \quad (22)$$

Oxidation-reduction reactions in acid solution often take place with the production (not consumption) of hydrogen ions. In such cases H^+ appears on the right side of the equation. The same is true in alkaline solutions except that here we are concerned with OH^- rather than H^+ ions.

Exercises

Complete and balance the following equations.

(The column on the right indicates the type of solution in which the reaction takes place. H^+ or OH^- may appear on either side of the equation and when neither is necessary the solution is designated as "neutral.")

	Reaction	*Solution*
1.	$MnO_4^- + Fe^{++} = Mn^{++} + Fe^{+++}$	H^+
2.	$MnO_4^- + Sn^{++} = Sn^{++++} + Mn^{++}$	H^+
3.	$Cr_2O_7^{--} + Fe^{++} = Fe^{+++} + Cr^{+++}$	H^+
4.	$Cr_2O_7^{--} + Sn^{++} = Sn^{++++} + Cr^{+++}$	H^+
5.	$CrO_4^{--} + HSnO_2^- = HSnO_3^- + CrO_2^-$	OH^-
6.	$H_2S + I_2 = S + I^-$	H^+
7.	$S_2O_3^{--} + I_2 = S_4O_6^{--} + I^-$	"neutral"
8.	$NO_3^- + Cu = Cu^{++} + NO$	H^+
9.	$SO_4^{--} + Cu = Cu^{++} + SO_2$	H^+
10.	$NO_3^- + Zn = Zn^{++} + NH_4^+$	H^+

	Reaction	*Solution*
11.	$H_2SO_3 + Fe^{+++} = Fe^{++} + SO_4^{--}$	H^+
12.	$CrO_2^- + ClO^- = Cl^- + CrO_4^{--}$	OH^-
13.	$MnO_4^- + H_2C_2O_4 = CO_2 + Mn^{++}$	H^+
14.	$H_2SO_3 + I_2 = SO_4^{--} + I^-$	H^+
15.	$CeO_2 + Cl^- = Ce^{+++} + Cl_2$	H^+
16.	$H_3AsO_4 + I^- = H_3AsO_3 + I_2$	H^+
17.	$O_2 + H_2O + I^- = I_2$	OH^-
18.	$CH_2O + Ag_2O = Ag + HCO_2^-$	OH^-
19.	$CH_2O + Ag(NH_3)_2^+ = Ag + HCO_2^- + NH_3$	OH^-
20.	$NO_3^- + Cu = Cu^{++} + NO_2$	H^+
21.	$NO_3^- + Ag = Ag^+ + NO_2$	H^+
22.	$NO_3^- + Ag = Ag^+ + NO$	H^+
23.	$NO_3^- + Fe^{++} = Fe^{+++} + NO$	H^+
24.	$NO_3^- + Zn = Zn^{++} + N_2$	H^+
25.	$NO_3^- + H_2S = S + NO_2$	H^+
26.	$BaO_2 + Cl^- = Cl_2 + Ba^{++}$	H^+
27.	$MnO_4^- + Br^- = Br_2 + MnO_2$	H^+
28.	$SO_4^{--} + I^- = I_2 + H_2S$	H^+
29.	$Cu^{++} + I^- = I_2 + Cu^+$	"neutral"
30.	$ClO^- + Mn(OH)_2 = MnO_2 + Cl^-$	"neutral"
31.	$Cl_2 = ClO_3^- + Cl^-$	OH^-
32.	$Fe^{+++} + H_2S = Fe^{++} + S$	H^+
33.	$NO_3^- + Fe = Fe^{+++} + NO$	H^+
34.	$ClO^- = ClO_3^- + Cl^-$	"neutral"
35.	$PbO_2 + Pb + SO_4^{--} = PbSO_4$	H^+
36.	$CN^- + MnO_4^{--} = CNO^- + MnO_2$	OH^-
37.	$CN^- + Fe(CN)_6^{----} = CNO^- + Fe(CN)_6^{----}$	OH^-
38.	$C_2H_4O + NO_3^- = NO + C_2H_4O_2$	H^+
39.	$NO_3^- + Cl^- = NOCl + Cl_2$	H^+
40.	$C_2H_3OCl + Cr_2O_7^{--} = Cr^{+++} + CO_2 + Cl^-$	H^+
41.	$CHCl_3 + MnO_4^- = Cl_2 + CO_2 + Mn^{++}$	H^+
42.	$Fe_3O_4 + MnO_4^- = Fe^{+++} + Mn^{++}$	H^+
43.	$SnS + S_2^{--} = SnS_3^{--}$	"neutral"
44.	$As_2S_3 + S_2^{--} = AsS_4^{---} + S$	"neutral"
45.	$Cu^{++} + CN^- = Cu(CN)_3^{--} + (CN)_2$	"neutral"
46.	$Hg_2Cl_2 + NH_3 = Hg(NH_2)Cl + Hg + NH_4^+ + Cl^-$	"neutral"
47.	$Ag^+ + AsH_3 = Ag + H_3AsO_3$	H^+
48.	$CrO_2^- + H_2O_2 = CrO_4^{--}$	OH^-
49.	$Sn^{++} + H_2O_2 = Sn^{++++}$	H^+

CHAPTER

6

Reaction Velocity and Chemical Equilibrium

In this chapter we shall be concerned with the problem of determining the extent to which chemical reactions take place and with the ways and means that are employed to control reactions and have them proceed as advantageously as possible. The problem can be stated more concretely by considering some specific example. For this purpose we shall choose the reaction

$$N_2 + 3H_2 = 2NH_3 \qquad (1)$$

In which direction does this reaction proceed at some specified temperature and pressure? At 1000° C and at a total pressure of one atmosphere, for example, will nitrogen react with hydrogen to form ammonia or will ammonia at this same temperature and pressure decompose into its constituent elements? From the results of experiment we know that at this temperature and pressure ammonia decomposes to a very large extent (practically completely) into nitrogen and hydrogen. Therefore, at one atmosphere pressure and at 1000° C nitrogen and hydrogen cannot combine appreciably to form ammonia.

At 450° C and one atmosphere pressure about 99.7 percent of the ammonia decomposes but in the absence of a catalyst it is necessary to wait a very long time before the reaction

reaches this point. Once this amount of decomposition has taken place, the reaction will proceed no further. This is the limit beyond which the reaction will not go. At 25° C it can be shown that only about 3 percent of the ammonia should decompose if the reaction proceeded rapidly enough. No means are known to the chemist of increasing the velocity of this reaction sufficiently to observe any change under these extreme conditions.

The limit to which any reaction can proceed is one of the important factors in determining its course. But it is apparent that there is another important factor controlling it, that of speed. These two factors, limit and speed, are sometimes confused when the "reactivity" of any substance or group of substances is considered. Reactivity usually refers to the velocity, or speed.

If only 3 percent of ammonia at 25° C and at one atmosphere pressure can decompose, then, conversely, hydrogen and nitrogen should combine at this same temperature and pressure to form ammonia, but this reaction also is not a feasible one because of its slow speed. Nitrogen is said to be nonreactive toward hydrogen in spite of the favorable limit of the reaction.

The subject of chemical equilibrium deals only with the limit or extent to which a reaction can take place. But a clear understanding of this subject demands a clear concept of reaction velocity and the factors which control it.

The Factors Controlling the Speed of a Reaction. Before two or more molecules can react they must collide with each other. But not every collision between reacting molecules is *effective*. In a vessel containing a mixture of hydrogen and oxygen at room temperature, billions of collisions occur each second between the molecules, yet no reaction occurs. Only those collisions which allow the molecules to penetrate deeply into each other result in reaction. This means that only collisions between fast moving molecules or between molecules having large energies with respect to each other will be effective. At room temperature there are not enough effective collisions between hydrogen and oxygen molecules to cause an

appreciable number to react. How can the number of effective collisions be increased?

Effect of Temperature. From our knowledge of the kinetic theory of gases and our concept of temperature, it is easy to predict that an increase in the temperature of the reactants will increase the speed of the reaction. By increasing the temperature the velocity of the molecules is increased. Consequently, at a higher temperature there are more effective collisions, and the number of such collisions increases very rapidly as the temperature is raised. Suppose, for example, that each effective collision must involve molecules which have fifty times as much energy with respect to each other as the average energy. In such a case one in every 10^{22} * collisions, as calculated from quantitative kinetic theory considerations, would be effective at 25° C. At 100° C there would be one effective collision in every 10^{17}, an increase of one hundred-thousand-fold in the number of effective collisions. While the *average* energy of the molecules does not increase very rapidly as the temperature is increased, the number of collisions involving large energies does. In the case just considered, we assumed that an effective collision required fifty times the average molecular energy. If the effective collision required only twenty times the average energy, then at 25° C one in every 10^{9} collisions would be effective and at 100° C one in about every 10^{7}. This time the number of effective collisions increases only one hundred times in going from 25° C to 100° C.

For a large proportion of all reactions the speed approximately doubles for every 10° rise in temperature. The process of cooking food involves chemical reactions. Most of these reactions proceed at about 100° C, the boiling point of water, but the cooking process can be hastened by the use of pressure cookers since, by not allowing the steam to escape, the temperature of the water can be increased beyond 100° C. When the vapor pressure of the water in the cooker is 25 lbs. per square inch in excess of that of the atmosphere, the temperature of the water is about 130° C. If the increase in the cooking

* For a discussion of exponential numbers refer to the Appendix.

speed doubles for every 10° rise, the speed at 130° C should be about eight times ($2 \times 2 \times 2$) that at 100° C. Conversely, when the cooking is done at high altitudes in open vessels, the speed of the cooking reaction is decreased, for at decreased atmospheric pressure water boils at a lower temperature.

When hydrogen and oxygen are heated to 500° C the reaction to form steam proceeds at a measurable rate. For this reaction the velocity more than doubles with every 10° rise in temperature, and at room temperature its rate is millions of millions of times slower. The combination of hydrogen with oxygen liberates a large amount of heat. If heat is generated faster than it can be removed, the reacting substances are raised to still higher temperatures and the reaction is further accelerated. This acceleration may take place in a fraction of a second and give rise to an explosion.

The burning of fuel such as wood also evolves heat. In this case the reaction does not get out of control but the heat evolved is sufficient to keep the burning material and the air above the *kindling* temperature. This reaction is a self-sustaining one, as are many of the reactions which evolve heat. When heat is absorbed by the reaction, the reaction cannot be self-sustaining. In this case heat must be supplied to the reactants.

Reactions involving ions, such as the neutralization of a strong acid by a strong base (see equation 10, Chapter 1), proceed very rapidly. For such reactions the ions have an attraction for each other and no excess energy is required for contact close enough to give rise to a reaction. Every collision or practically every collision between the ions is an effective one.

Effect of Concentration. By increasing the concentration of all or any of the reacting substances, the velocity of a reaction increases. With increased concentration any one molecule has a greater chance of colliding with another with which it may react. Hydrogen does not react as rapidly with air which is one-fifth oxygen as it does with pure oxygen. Also, a mixture of hydrogen and oxygen at very low pressures reacts

more slowly than at high pressures. In fact, a mixture of hydrogen and oxygen does not explode when ignited if the total pressure of the mixture is sufficiently low. In any reaction taking place between two reactants, doubling the concentration of any one reactant doubles the number of total collisions and also doubles the number of effective collisions. Doubling the concentration of both reactants quadruples the number of collisions.

The reaction between gaseous iodine and hydrogen to form gaseous hydrogen iodide may be considered as an example to illustrate the effect of concentration on the speed of the reaction.

$$H_2 + I_2 = 2HI \qquad (2)$$

Consider first the reactants under conditions of temperature and concentration (or pressure) which allow a measurable reaction speed. If the hydrogen concentration is now doubled and the concentration of the iodine kept the same, the reaction speed will be doubled, for now each iodine atom will make twice as many collisions with hydrogen atoms, hence twice as many effective collisions. The same result would be obtained by doubling the concentration of iodine and keeping the concentration of the hydrogen the same as it was originally. If now both the concentration of the hydrogen and the concentration of the iodine are doubled, the number of effective collisions will be increased fourfold and the speed of the reaction will be four times as great This concept will be developed more fully in the latter part of this chapter.

Effect of a Catalyst. The speed of many reactions is increased by the presence of some substance which itself undergoes no permanent chemical change during the reaction. Such a substance is known as a ***catalyst.*** Catalysts may be divided into two general classes: (1) contact catalysts, and (2) those which form intermediate substances which in turn react to regenerate the catalyst. The reaction of sulfur dioxide with oxygen to form sulfur trioxide in the presence of nitric oxide is an example of the latter class. Oxygen does not react with sulfur dioxide with any appreciable speed at 500° C when no

other substance is present, yet in the presence of nitric oxide, NO, this reaction proceeds rapidly. The nitric oxide itself combines readily with oxygen and the product formed, NO_2, then reacts with the sulfur dioxide forming sulfur trioxide and regenerating the nitric oxide for further uses as a catalyst. Known catalysts of this type are far fewer than contact catalysts.

Contact catalysts are those which provide a surface upon which the reacting substances may come in contact with each other. The catalyst has the ability to hold (adsorb), a monomolecular layer of one or more of the reactants on its surface. When the reactant is thus adsorbed, the field of force about the adsorbed reacting molecule is so changed that the molecule with which it is to react does not have to penetrate so deeply to cause reaction. More of the collisions are therefore effective, hence the speed of the reaction is increased. Finely divided platinum is used as a catalyst for many reactions, among which are the oxidation of sulfur dioxide to sulfur trioxide (contact process of making sulfuric acid), the addition of hydrogen to unsaturated organic compounds (hydrogenation of cottonseed oil, for example), the oxidation of methanol to formaldehyde ($2CH_3OH + O_2 = 2CH_2O + 2H_2O$), the reaction between nitrogen and hydrogen to form ammonia, the oxidation of carbon monoxide to carbon dioxide, and the reaction between hydrogen and oxygen to form water. Since the function of the platinum is to provide an active surface, the greater the surface area of the catalyst the greater is its effectiveness. The surface of the catalyst is increased by spreading the platinum over some other inert substance such as asbestos. This can be done by soaking asbestos in a solution of a platinum salt and then decomposing the salt by heat. For commercial practice a substitute for platinum is usually sought because of the high cost of the metal.

Heterogeneous and Homogeneous Reactions. All reactions may be classified as either ***heterogeneous*** or ***homogeneous.*** Those which take place at some surface are the heterogeneous reactions, examples of which were cited in the

last section. In some cases the surface itself may be one of the reactants. The rusting of iron, for example, is a heterogeneous reaction in which the surface of the iron reacts with the oxygen. In this case one of the reactants is a gas and the other a solid. When manganese dioxide is placed in a solution of hydrogen peroxide, the latter substance decomposes to give water and oxygen. The manganese dioxide acts as a catalyst and the reaction is a heterogeneous one When copper sulfate solution reacts with zinc to give zinc sulfate solution, it is the copper ion in solution which is involved in the reaction with the zinc to give zinc ions and metallic copper This reaction also is a heterogeneous one.

Reactions which do not take place on a surface or at an interface between two different phases are called homogeneous reactions. In homogeneous reactions all reactants are gases, liquids in the same solution, or solids dissolved in each other. In other words, for homogeneous reactions there is no boundary surface between the reactants nor do the reactants combine with each other on the surface of a catalyst The burning of illuminating gas is an example of a homogeneous reaction. All the reactants, the gas and the oxygen of the air are gaseous (of the same phase) and the reaction does not take place on a surface. However, when this reaction takes place on a Welsbach mantle, the mantle acts as a catalyst and the reaction is then a heterogeneous one. When gaseous hydrogen reacts with gaseous iodine to form gaseous hydrogen iodide (equation 2), the reaction is a homogeneous one since all the constituents are confined to a single phase.

Reactions Involving Ions. When a barium chloride solution is added to a solution of sodium sulfate a precipitate of barium sulfate immediately forms. Barium ions and the sulfate ions must eventually attach themselves to the surface of the crystal in their regular places to form the crystal of barium sulfate. The crystal of barium sulfate grows by deposition on its surface and part of the reaction at least must be heterogeneous.

The formation of the crystal nucleus, that is, the attach-

ment of the first ions to each other, is a different kind of a reaction. Perhaps that part of the reaction is a homogeneous one. The phenomenon of supersaturation attests to the fact that this part of the reaction is different. In a supersaturated solution of sodium thiosulfate, for example, the rate of formation of crystal nuclei is so slow that crystallization cannot set in. If a crystal of solid sodium thiosulfate is added to such a solution, crystallization immediately occurs. In most ionic reactions, however, the rate of formation of crystal nuclei is very fast, as is crystallization once nuclei have been formed.

The neutralization of a solution of sodium hydroxide by a solution of hydrochloric acid is an example of a homogeneous ionic reaction. As was previously stated, this reaction involves the combination of the hydrogen and hydroxide ions to form water and is confined to a single phase. The ionization of any weak acid or weak base in water solution is a homogeneous reaction of the ionic type.

Reversible Reactions. The formation of water by the combination of hydrogen with oxygen has previously been used to illustrate the different factors to be considered in an understanding of reaction velocity. It has been stated that these two elements react with each other almost completely at moderate temperatures. On the other hand, at 2000° C or above, an appreciable amount of steam is broken up into hydrogen and oxygen. Even at room temperature we may assume that some water vapor molecules dissociate into hydrogen and oxygen, but that the rate of dissociation and its extent are so small that the change cannot be detected. All reactions may be regarded as reversible. Often the amount of reversibility is so small that it cannot be determined by any known experimental method, but it would be contrary to our ideas concerning probability to suppose that any chemical reaction is absolutely irreversible. However, when no detectable amount of reversibility is ever observed it is common practice to regard the reaction as "irreversible."

When sodium reacts with water, hydrogen and a solution of sodium hydroxide are produced:

$$2Na + 2H_2O = 2NaOH + H_2 \quad (3)$$

If the reverse process of passing hydrogen into a solution of sodium hydroxide is carried out, no detectable amount of sodium is produced, yet we may not say that not even a single atom of sodium is formed in such a process. If we were to be entirely practical, we would regard such a process as irreversible, yet from the standpoint of equilibrium, the subject we are to consider next, it will be very useful to regard every chemical reaction as having some tendency to reverse itself, however small that tendency may be.

Chemical Equilibrium. The reaction

$$2NH_3 = N_2 + 3H_2 \quad (4)$$

was previously used to show that there is a definite limit beyond which a reaction cannot proceed. At the time the example was given, it was not made apparent why the reaction stopped before completion, but it was by no means implied that the reaction suddenly comes to a standstill. The reason for the definite limit is that the NH_3 is simultaneously being formed and finally a condition is reached in which the two opposing reactions proceed at the same rate. In this state of balance the amounts of NH_3, N_2, and H_2 present in the reaction mixture remain constant.

This condition of equilibrium, which any chemical reaction can attain, can be likened to a horse running on a treadmill which moves faster as the horse increases his speed. When the horse and the treadmill are in equilibrium, the horse is apparently stationary to an observer. If the horse runs faster, he advances a few feet, but the mill also moves faster and again he appears to be stationary, although his stationary position will be in advance of his previous one. In the case in which the reaction just considered is in equilibrium the amount of NH_3, N_2, and H_2 remains constant, yet like the horse and the treadmill the reactions proceed in opposite directions with the same speed. At equilibrium the forward and reverse reactions always proceed at the same rate.

The Law of Mass Action. The Law of Mass Action is a quantitative statement relating the velocity of a reaction to the concentrations of its reactants. To develop the quantitative notions of chemical equilibrium, that is, to understand the Law of Mass Action, we shall consider the hypothetical reaction

$$A + B = C + D \tag{5}$$

In this reaction A molecules react with B molecules to form C and D molecules. For the A and B molecules to react it is necessary that they collide with each other. The number of molecules reacting in a given time will be proportional to the number of collisions between them. If the number of collisions between A and B molecules in one case were twice as great as that in another in a given time, then twice as many A and B molecules would react. To determine the dependence of the rate of the reaction upon the concentrations of A and B, it is only necessary to determine the manner in which the number of collisions between A and B molecules varies with their respective concentrations. To do this, consider a closed vessel containing only A and B molecules and for simplicity, suppose that there are only 4 A molecules and 4 B molecules present in the vessel. Let us determine the chance that any A molecule will collide with a B molecule in a given time. We arbitrarily indicate the chance of collision by drawing lines between A and B molecules (Figure 6.1). Under the conditions we have chosen, the chance that any A molecule will collide with any B molecule is 16 (16 lines). Each A molecule has 4 chances of colliding with a B molecule and since there are 4 A molecules the total chance becomes 4×4 or 16. It is obvious that collisions between like molecules are not to be included since they do not lead to reaction in this case.

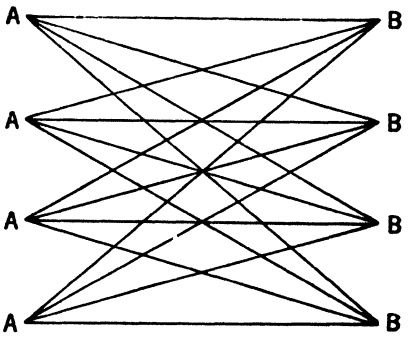


FIG. 6.1

Now suppose the concentration of A molecules is doubled, that is, there are 8 A molecules and 4 B molecules in the same container (Figure 6.2). The chance that any A molecule will collide with any B molecule will now be 32 (4×8 lines). The number of A molecules in the second case is now twice that in the first and the chance for collision between the A and B

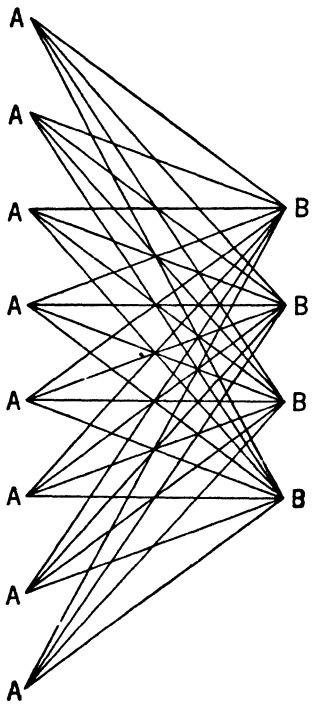


FIG. 6.2

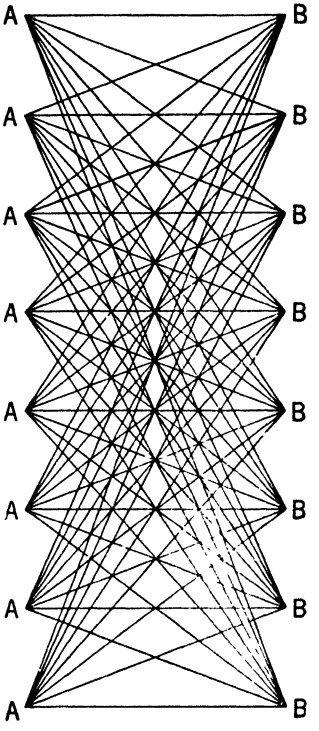


FIG. 6.3

molecules is doubled. With 8 A molecules and 8 B molecules (Figure 6.3), the chance of collision is 64 (8×8 lines). In general, the chance of collision will be equal to $N_a \times N_b$, where N_a and N_b represent the number of A and B molecules respectively.

In all of the above cases the size of the container was the same, so N_a, expressed in proper units, is the concentration of A molecules, and N_b the concentration of B molecules. The

chance for collision between A and B molecules is then proportional to the *product of the concentrations of A and of B molecules*. But the rate of the reaction is directly proportional to the number of collisions. Therefore, the rate at which A molecules combine with B molecules is also proportional to the *product of the concentrations of A and B*.

$$\text{Rate}_1 \sim (A) \times (B) \tag{6}$$

or

$$\text{Rate}_1 = k_1(A) \times (B) \ * \tag{7}$$

where (A) and (B) represent the concentrations of A and B respectively, and k_1 is a proportionality constant.

Let us now consider the reverse reaction

$$C + D \rightarrow A + B \tag{8}$$

By the same argument it can be shown that the rate of this reaction is proportional to the product of the concentration of the C molecules and the concentration of the D molecules, that is,

$$\text{Rate}_2 = k_2(C) \times (D) \tag{9}$$

where (C) and (D) now represent the concentrations of C and D molecules, and k_2 is a proportionality constant.

When the system is in equilibrium both the reactions proceed simultaneously,

$$A + B = C + D \tag{10}$$

and the rate in the forward direction is equal to the rate in the backward direction,

$$\text{Rate}_1 = \text{Rate}_2 \tag{11}$$

or

$$k_1(A) \times (B) = k_2(C) \times (D) \tag{12}$$

and

$$\frac{k_1}{k_2} = \frac{(C) \times (D)}{(A) \times (B)} \tag{13}$$

Since k_1 and k_2 are both constants, the ratio $\frac{k_1}{k_2}$ is also a constant.

$$\frac{(C) \times (D)}{(A) \times (B)} = K_{eq} \tag{14}$$

* See discussion of proportion and proportionality constants in the Appendix.

K_{eq} is known as the equilibrium constant for the reaction. This expression means that the concentrations of all four substances are so related that if the concentration of any one is changed, the concentrations of the others must vary through a chemical reaction in such a way as to make the value of the expression $\frac{(C) \times (D)}{(A) \times (B)}$ the same as it was originally.

Let us now consider another hypothetical case in which we have two molecules of the same kind reacting with each other, for example,

$$2A \rightarrow C + D \tag{15}$$

Two molecules of A react with each other to form one molecule of C and one of D. This time we shall determine the chance of collision between any two A molecules. Suppose there are 6 A molecules in the enclosed vessel. Counting the chances as was done in the previous case we find that there are 15 ($5 + 4 + 3 + 2 + 1$ lines, Figure 6.4), that is, the first molecule to be considered has 5 chances of collision, the next molecule has 4 chances (not counting the same chance twice), the third molecule, 3 chances, etc.

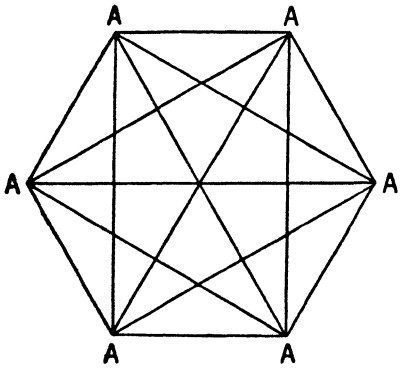


FIG. 6.4

If we double the number of A molecules (now 12), we find that the chance is 66 ($11 + 10 + 9 + 8 + 7 + 6 + 5 + 4 + 3 + 2 + 1$ lines). In general, for N molecules the chance of collision will be $(N - 1) + (N - 2) + (N - 3) + \cdots + 1$. The mathematical formula for determining the sum of such a series of combinations is

$$\frac{(N - 1)N}{2} \tag{16}$$

Therefore, the number of collisions is proportional to $(N - 1) \times N$. N represents the number of molecules in the

system. For all actual cases N is an exceedingly large number, so $(N-1)$ may be considered equal to N, and $(N-1) \times N$ is practically equal to N^2. When we recall that the lowest vacuum we can possibly obtain still contains billions of molecules per cubic centimeter, certainly one molecule more or less can make no appreciable difference, so we are quite justified in letting $N-1$ equal N. Accordingly, we may say that the number of collisions in such a case is proportional to N^2. But since N may be expressed as the concentration of the reacting substance, in this case A molecules, the number of collisions is proportional to the concentration of A molecules squared. For this case,

$$\text{Rate}_1 = k_1(A)^2 \tag{17}$$

The reverse reaction,

$$C + D \rightarrow 2A \tag{18}$$

is similar to that already considered in the first case, and for this reaction it was shown that

$$\text{Rate}_2 = k_2(C) \times (D) \tag{19}$$

For equilibrium,

$$2A \rightleftharpoons C + D \tag{20}$$

and

$$\text{Rate}_1 = \text{Rate}_2 \tag{21}$$

Consequently,

$$\frac{k_1}{k_2} = \frac{(C) \times (D)}{(A)^2} = K_{eq} \tag{22}$$

In this case it will be noted that the equilibrium expression involves the concentration of A to the second power.

The two hypothetical cases considered are relatively simple but more complicated reactions offer no special difficulty. Thus, for the equilibrium,

$$2A + B \rightleftharpoons 2C + D \tag{23}$$

we may think of the forward reaction as taking place in two steps, the first step resulting in the formation of some intermediate compound, say A_2, which in turns reacts with B,

$$2A \rightarrow A_2 \tag{24}$$

and

$$A_2 + B \rightarrow 2C + D \tag{25}$$

The net result is the sum of equations (24) and (25),

$$2A + B \rightarrow 2C + D$$

which is the forward reaction of (23). Therefore the rate of the forward reaction is proportional to $(A)^2 \times (B)$ or

$$\text{Rate}_1 = k_1(A)^2 \times (B) \tag{26}$$

In a similar manner the reverse reaction may be thought of as taking place in two steps, and

$$\text{Rate}_2 = k_2(C)^2 \times (D) \tag{27}$$

At equilibrium, where $\text{Rate}_1 = \text{Rate}_2$,

$$\frac{(C)^2 \times (D)}{(A)^2 \times (B)} = K_{eq} \tag{28}$$

The same result could be obtained by assuming that some other intermediate compound, such as AB, is formed by the reaction

$$A + B \rightarrow AB \tag{29}$$

which in turn reacts with A,

$$AB + A \rightarrow 2C + D \tag{30}$$

In fact, it is not even necessary to assume the formation of any intermediate compound, but rather to consider the collisions between two A molecules and one B molecule simultaneously. In this case the rate in the forward direction would be proportional to the number of B molecules times the number of collisions between two A molecules. Since the number of collisions between two A molecules is proportional to $(A)^2$, then the number of collisions between two A molecules and one B molecule will be proportional to $(N_a)^2 \times N_b$. By the same arguments used previously,

$$\text{Rate}_1 = k_1(A)^2 \times (B) \tag{31}$$

and the same result for the equilibrium expression could be obtained.

In general, for the reaction

$$nA + mB \rightleftharpoons pC + rD \tag{32}$$

where n, m, p, and r are small whole numbers, the expression for the equilibrium constant will be

$$K_{eq} = \frac{(C)^p \times (D)^r}{(A)^n \times (B)^m} \tag{33}$$

Expressed in mathematical language this is a generalized statement of the Law of Mass Action or the Law of Chemical Equilibrium.

In this expression it will be observed that the concentration of each reacting substance is raised to the same power as the coefficient of the respective term in the equation representing the reaction. According to convention the concentrations of the substances in the numerator of this expression are for those substances on the right side of the equation as written (products of the forward reaction), and the concentrations in the denominator are those for the substances on the left side of the equation (reactants).

Factors Influencing Equilibrium. Since at equilibrium a chemical reaction is proceeding in the forward and backward directions with equal velocities, it might be expected that those factors, such as temperature and concentration, which affect the speed of any reaction might also affect the equilibrium; that is, it might be expected that these same factors might change the balance between the two opposing reactions. To understand the problem more clearly, it might be advantageous again to consider the analogy between a chemical system in equilibrium and the horse running on a treadmill which increases its speed as the horse advances. If the horse, while running and apparently remaining stationary with respect to some fixed point, is spurred forward by a whip, he increases his speed and advances; but as he does so the speed of the treadmill also increases and again the horse comes to an apparently stationary position. For the second time, the horse and treadmill are in a state of equilibrium, but the horse has now occupied a position farther forward. If, on the other hand, a load is hitched to the horse he runs slower. Momentarily he shifts his position backward, but since the treadmill runs

slower he soon assumes a new position of equilibrium. During the short interval that the horse advances or falls back the position of equilibrium is shifted.

In an analogous manner, the equilibrium position of a chemical reaction may be shifted, and it is common to speak of a ***shift in equilibrium*** to the right or to the left with reference to the chemical equation for the reaction taking place. Thus for the equilibrium between sulfur dioxide, oxygen and sulfur trioxide as represented by the equation

$$2SO_2 + O_2 = 2SO_3 \qquad (34)$$

all these substances are present in definite quantities and the reaction is proceeding in both directions. If now, by some influence, the equilibrium is shifted so that more sulfur trioxide is formed, we say that the equilibrium is *shifted to the right.* During the change from one equilibrium position to another the reaction proceeds momentarily faster from left to right than from right to left. The situation is analogous to the momentary shift in the position of the horse on the treadmill when he is spurred to a faster speed. With this explanatory introduction we may state the problem of this chapter more precisely. What factors shift the equilibrium of a chemical system of reacting substances?

The Effect of Changing the Concentration. The equilibrium existing in a chemical system may be shifted by increasing the speed of either the forward or backward reaction. In the hypothetical reaction

$$A + B = C + D \qquad (35)$$

the forward speed depends upon the product of the concentrations of the A and B molecules while the speed of the backward reaction depends upon the product of the concentrations of the C and D molecules. If, when the system is in equilibrium, an additional amount of A or B is added, the forward rate is increased because the concentration of the reacting molecules is increased. The forward rate will momentarily be greater than the reverse rate; the system is temporarily out of equilibrium

and C and D molecules will be produced faster than they disappear. But as the concentrations of C and D increase the reverse rate also increases until eventually it again becomes equal to the forward rate. A new state of equilibrium is attained. The addition of an extra amount of either A or B is like applying a whip to the horse on the treadmill. In the same manner that the horse moves forward, the equilibrium position shifts from left to right. In the second state of equilibrium the substances on the right side of the equation are present in greater concentration than originally. By increasing the concentration of either or both C and D the equilibrium can likewise be shifted to the left.

The equilibrium may also be shifted to the right by removal of either C or D. In this case the reaction from right to left is momentarily retarded and the reaction from left to right proceeds faster than that from right to left until a new equilibrium condition is again reached.

These same conclusions may be drawn by a consideration of the equilibrium constant. For the hypothetical reaction (35)

$$\frac{(C) \times (D)}{(A) \times (B)} = K_{eq} \tag{36}$$

If, when the system is in equilibrium, the concentration of A is increased, then momentarily the value of the above expression would be smaller than K_{eq}. The system must then shift so as to make the expression equal to K_{eq}. When this is done (C) and (D) increase and (B) decreases. In other words, some B molecules react with some of the A molecules that were added to form more C and D molecules.

In general, if the concentration of one of the substances appearing on the right side of the equation is increased, the equilibrium shifts from right to left and vice versa. If the concentration of one of the substances on the right side of the equation is decreased, the equilibrium shifts from left to right.

The Rule of Le Chatelier. The effect of concentration on equilibrium, just discussed in the last section, is a special case of the general theorem known as the ***Rule of Le Chatelier.***

This rule states that, for a system already in equilibrium, any change in the factors which affect this equilibrium will cause the system to shift in such a way as to neutralize the effect of this change.

The total pressure to which a system is subjected is often one of the factors affecting equilibrium. According to the Rule of Le Chatelier, if the total external pressure is increased, the system will change in such a way as to reduce this effect, that is, the equilibrium will shift so as to decrease the pressure. For a gaseous system, the shift will take place in such a way as to decrease the total number of molecules, for this would result in a smaller pressure. This effect of pressure may be illustrated by the reaction

$$2NO_2 = N_2O_4 \tag{37}$$

Consider the substances, represented by the formulae in this equation, to be in equilibrium and to be exerting a definite total pressure on the wall of the container. If the external pressure is increased, it will be momentarily balanced by the pressure exerted by the N_2O_4 and the NO_2. But by the Rule of Le Chatelier the system will change to a condition which will reduce the effect of the increased pressure. That is, the above equilibrium will shift in the direction of a fewer number of molecules, for two NO_2 molecules are required to produce one N_2O_4. In other words, an increase in the external pressure will shift the equilibrium to the right. Conversely, a decrease in total pressure (by expansion) will shift the equilibrium from right to left.

In the system consisting of ice and water in equilibrium at 0° C as much ice melts as is formed. This is an example of a physical equilibrium but it may be treated in the same manner as a chemical equilibrium. Therefore we may write

$$\text{ice} = \text{water} \tag{38}$$

If pressure only is now applied to the system, water in equilibrium with ice, the system will change in such a way as to make the volume smaller, thereby reducing the pressure

exerted on the sides of the container by its contents. Since water occupies a smaller volume than an equivalent amount of ice, some ice will melt as pressure is applied. However, as the ice melts it absorbs heat. The temperature will therefore drop and a new state of equilibrium will be reached. The melting point of ice decreases with increased pressure.

If a system of molecules in equilibrium in solution is diluted, the equilibrium will shift in such a way as to decrease the effect of dilution; that is, it will shift so as to produce more molecules or particles. Acetic acid is a weak acid which in solution consists of acetic acid molecules in equilibrium with its dissociation products, hydrogen ion and acetate ion, in accordance with the equation

$$HC_2H_3O_2 = H^+ + C_2H_3O_2^- \qquad (39)$$

Dilution decreases the concentrations of all substances but this dilution effect will be counterbalanced by the production of more particles; that is, the above reaction will shift from left to right. Conversely, if the solution is concentrated by evaporation the above equilibrium will shift from right to left.

The Effect of Temperature on Equilibrium. Let us now consider the effect on equilibrium of changing the temperature. Increasing the temperature of a reacting system in equilibrium will increase the velocities of the reactions in both directions. If the forward and backward reactions were increased by exactly the same amount by an increase in temperature there would be no change in the position of equilibrium. Returning to the analogy of the horse on the treadmill, an increase in temperature is like increasing both the speed of the horse and the mill. If the speeds of both increase by exactly the same amount the horse will remain in an apparently stationary position. If, however, the speed of the horse is increased to a greater extent than that of the mill, the horse will move forward to a new equilibrium position. Likewise, if the speeds of the forward and backward reactions are not increased by the same amount, a shift in the equilibrium position will occur.

The effect of temperature on equilibria can best be judged

from the standpoint of the Rule of Le Chatelier. When any reaction proceeds in one direction, from right to left or vice versa, heat is either evolved or absorbed. Thus, when carbon monoxide reacts with oxygen to form carbon dioxide heat is evolved. This effect may be included in the equation

$$2CO + O_2 = 2CO_2 + \text{heat} \tag{40}$$

If, when all these substances are in equilibrium, the temperature is increased or heat is applied, the equilibrium will shift in such a way as to absorb the heat; that is, the equilibrium will shift from right to left, for proceeding in this direction the reaction absorbs heat. At higher temperatures, then, more CO_2 is dissociated into CO and O_2 at equilibrium than at lower temperatures.

While changing the concentration of one of the reactants and keeping the temperature constant shifts the equilibrium, it does not change the value of the equilibrium constant. The effect of temperature change, however, is to alter the value of the constant. The equilibrium expression for the reaction just considered is

$$\frac{(CO_2)^2}{(CO)^2(O_2)} = K_{eq} \tag{41}$$

K_{eq} has a definite value for each temperature and it may be deduced that the higher the temperature the lower the value of the constant. (Lower values of K_{eq} correspond to a smaller concentration of CO_2 and a larger concentration of CO and O_2.)

Catalysts Cannot Shift Equilibrium. While catalysts are used to increase the speed of a reaction, they cannot shift its equilibrium position. It can be demonstrated that a shift in chemical equilibrium by a catalyst would be equivalent to a perpetual motion machine. It would only be necessary to bring the catalyst alternately in and out of the reaction mixture. Knowing that perpetual motion is impossible, we must conclude that a catalyst cannot influence the equilibrium position. The complete argument is one which falls into the scope of chemical thermodynamics and cannot be given here.

If a catalyst can increase the velocity of a reaction but not

affect its equilibrium it must follow that a catalyst which increases the speed of a forward reaction also increases the speed of the reverse reaction by an equal amount. This deduction has been verified many times by experiment. Specially prepared iron, which is a good catalyst for the formation of ammonia from hydrogen and nitrogen is also a good catalyst for the decomposition of ammonia into its elements (the reverse of the formation reaction).

Questions and Problems

1. Deduce from kinetic theory considerations that an increase in temperature will cause an increase in the velocity or rate of any given reaction.
2. If the velocity of a reaction doubles for every ten degree rise in temperature, how much faster would the reaction proceed at 100° C than at 20° C?
3. On the basis of the increase of reaction rate with increase of temperature explain why a mixture of hydrogen and oxygen explodes when ignited.
4. How much faster will the reaction, $H_2 + I_2 \rightarrow 2HI$, proceed if the partial pressures of the H_2 and I_2 are two atmospheres each than it will if their partial pressures are each one-half atmosphere (at the same temperature)?
5. What are the two classes of catalysts?
6. What is the distinction between a heterogeneous and a homogeneous reaction?
7. Is the neutralization of an acid solution by a basic solution a heterogeneous or homogeneous reaction?
8. What is meant by the term "irreversible reaction"?
9. If SO_2, O_2 and SO_3 are in equilibrium, has all reaction stopped either in the forward or reverse direction? The equation is

$$2SO_2 + O_2 = 2SO_3$$

Explain.

10. Show that for equilibrium for the hypothetical reaction

$$A + B = C + D$$

the concentrations of A, B, C and D must satisfy the condition that $\frac{(C) \times (D)}{(A) \times (B)}$ is equal to a constant.

11. If 5 molecules of the same kind in a given container make on the average ten collisions with each other every second, how many collisions per second would occur if 15 molecules instead of 5 were present?

12. In the equation $\frac{a \times b}{c \times d} = K$, where K is a constant, let the values of a, b, c and d be 3, 4, 5 and 6 respectively. What is the value of K? In each of the following cases determine the value of a, b, c or d from the value of K obtained previously and from the values of the other three letters; i.e., fill in the blanks to make the value of K the same as that previously obtained.

	a	b	c	d
(1)	3	4	10	..
(2)	3	4	20	..
(3)		4	5	3
(4)	.	4	5	12
(5)	3	.	5	12
(6)	3	..	5	24
(7)	6	8	5	..
(8)	12	16	5	..

13. Write the expression for the equilibrium constant for each of the following reactions:

(1) $HCN = H^+ + CN^-$
(2) $NH_4OH = NH_4^+ + OH^-$
(3) $H_2S = 2H^+ + S^{--}$
(4) $Hg_2^{++} + 2Fe^{+++} = 2Fe^{++} + 2Hg^{++}$
(5) $CO_2 + H_2 = CO + H_2O$ (gas)
(6) $2NO_2 = 2NO + O_2$
(7) $3H_2 + N_2 = 2NH_3$ (gas)

14. Consider the system represented by the equation

$$N_2 + 3H_2 = 2NH_3 + \text{heat}$$

to be in equilibrium.
(a) What will be the effect of adding more H_2 to the system? (Will the equilibrium shift to the right or left or remain stationary?)
(b) What will be the effect of adding more NH_3?

(c) What will be the effect of increasing the total pressure?
(d) What will be the effect of increasing the temperature?

15. What is the Rule of Le Chatelier?

16. Explain why a catalyst which accelerates the rate of a reaction in one direction must also accelerate the rate in the reverse direction.

17. At 60° C the solubility of KNO_3 is 110 g. per 100 g. of water, while at 20° C its solubility is 26 g. per 100 g. of water. Is heat liberated or absorbed when KNO_3 is dissolved?

18. When NH_4NO_3 dissolves in water heat is absorbed. Is NH_4NO_3 more or less soluble at high than at low temperatures?

19. In the game of pocket billiards there are, besides the "projectile" ball or cue ball, fifteen other balls numbered 1 to 15. The score of any player is determined by the summation of numbers of the balls he pockets (the balls must be pocketed in successive order). If any one player should pocket all the balls, show by equation (16) that his score will be 120. Confirm this result by adding all numbers from 1 to 15, inclusive.

CHAPTER

7

Equilibria Involving Weak Acids and Bases

In the previous chapter we considered a generalized treatment of the Law of Mass Action or the Law of Chemical Equilibrium, which for liquid systems can be applied only to solutions of relatively insoluble substances or to solutions of weak electrolytes. Although relatively few of the known substances belong to this latter class, the majority being either strong electrolytes or non-electrolytes, yet from the standpoint of chemical equilibrium the weak electrolytes are of the greatest importance and henceforth we shall deal to a very large extent with equilibria involving this class of compounds.

Of all the weak electrolytes weak acids are the most important, not only in the subject of qualitative analysis and in problems of a purely chemical nature but also in biological systems involving the blood, the tissue and cell materials, and the glandular secretions. In many systems it is highly important that not only the hydrogen ion concentration be controlled but that a source of hydrogen ions be at hand to replace those which may be used up. The molecules of weak acids act as such a source of hydrogen ions for, as we shall see, the Law of Mass Action demands that as hydrogen ions are removed by chemical reaction, more molecules must dissociate to replace the ions that may be consumed.

The neutralization of both a strong and a weak acid by a

solution of sodium hydroxide may be used to illustrate the action of a weak acid as a hydrogen ion reservoir. Hydrochloric acid and acetic acid, CH_3COOH, are typical examples of strong and weak acids respectively. Hydrochloric acid in a 1 molar solution is completely dissociated and the concentrations of the hydrogen ion and chloride ion are each 1 molar. Acetic acid in a 1 molar solution, on the other hand, is dissociated only to the extent of about 0.43 percent, so the hydrogen ion concentration in this solution is only .0043 molar. In spite of the difference in the hydrogen ion concentrations in the two cases cited, equal quantities of these two solutions will require the same amount of sodium hydroxide to neutralize them. When the sodium hydroxide solution is added to the solution of hydrochloric acid the reaction taking place is simply the combination of hydrogen ions and hydroxide ions of the acid and base respectively to form water, as represented by the equation

$$H^+ + OH^- = H_2O \qquad (1)$$

When sodium hydroxide is added to the solution of acetic acid we may regard the reaction as being made up of two steps or two parts. In the first place, we may regard the free hydrogen ions as combining with the hydroxide ions, the same reaction as with hydrochloric acid. As the hydrogen ions are removed, more acetic acid dissociates.

$$CH_3COOH = H^+ + CH_3COO^- \qquad (2)$$

This dissociation and combination proceeds until all the acetic acid molecules have been used up, and therefore the amount of sodium hydroxide required in the two cases will be the same. The over-all reaction for the neutralization of acetic acid by sodium hydroxide represents the summation of these two steps and is written

$$CH_3COOH + OH^- = CH_3COO^- + H_2O \qquad (3)$$

The acetic acid in solution consists principally of CH_3COOH molecules, and since it is these molecules which ultimately disappear during the course of the reaction, CH_3COOH, and

not H^+ as in equation (1), must appear on the left side of the equation.

In later chapters we shall see how it is possible to calculate the hydrogen ion concentration after any given amount of sodium hydroxide has been added to the acetic acid solution. Also, in a later chapter we shall briefly discuss the rôle of weak acids in controlling the hydrogen ion concentration in the blood.

The Ionization of Weak Acids. To illustrate the application of the Law of Chemical Equilibrium to weak acids, let us consider again acetic acid and its ions in solution. The acetic acid molecules are in equilibrium with the hydrogen ions and acetate ions, which equilibrium may be expressed by the equation

$$HAc = H^+ + Ac^- \qquad (4)$$

Applying the Law of Chemical Equilibrium to this case we find that $\frac{Conc.\ H^+ \times Conc.\ Ac^-}{Conc.\ HAc}$ equals a constant. In a more abbreviated form this is written

$$\frac{(H^+)(Ac^-)}{(HAc)} = K_I \qquad (5)$$

K_I is known as the Ionization Constant. In any Law of Mass Action expression the concentrations of the substances involved in the expression are given in terms of moles per liter, never as grams per liter or as grams per 100 ml.

In a 0.1 molar solution of acetic acid the concentrations of the H^+ and Ac^- ions are the same, and by experiment we know that their concentrations are each .00135 molar. The concentration of the undissociated acid must be $0.1 - .00135$ or .09865 molar, since the total of dissociated and undissociated acid must equal 0.1 molar. (Note that the amount of undissociated acid is $0.1 - .00135$ and not $0.1 - 2 \times .00135$, as a too hasty deduction might lead one to believe. Each molecule which dissociates produces one hydrogen ion and one acetate ion. A concentration of .00135 molar of either hydrogen ions

or acetate ions in this case means that .00135 moles of acetic acid molecules are dissociated in one liter of solution.) The numerical value of the foregoing expression then becomes

$$\frac{(H^+)(Ac^-)}{(HAc)} = \frac{.00135 \times .00135}{.09865} = .0000185 \text{ or } 1.85 \times 10^{-5}$$

The value of K_I at 25° C is then 1.85×10^{-5}. At any other temperature acetic acid is not dissociated to the same extent. At 100° C, for example, the dissociation constant for acetic acid is 1.1×10^{-5}. In other words, the value of 1.85×10^{-5} holds for the temperature of 25° C only. However, at this temperature K_I has the same value for solutions other than 0.1 molar. For a .01 molar solution, for example, the same value of K_I is obtained. From this value of K_I it is now possible to calculate the concentrations of the H^+ and Ac^- ions in any solution of acetic acid which is not too concentrated.

In a .01 molar solution of acetic acid the total amount of acetic acid, both dissociated and undissociated, contained in one liter is .01 mole. If we let X be the concentration of the H^+ ion, then the concentration of the Ac^- ion is also X and the concentration of the undissociated acid is $.01 - X$. Then,

$$\frac{(H^+)(Ac^-)}{(HAc)} = \frac{X^2}{.01 - X} = 1.85 \times 10^{-5} \qquad (6)$$

In solving this equation for the value of X (the H^+ and Ac^- concentrations), let us first assume that X is very small as compared with .01; so small that the amount of undissociated acid $(.01 - X)$ is practically equal to .01. (X can be neglected in such equations only when it is added to or subtracted from some other number much larger than X. It cannot be neglected in the numerator of the foregoing expression.) The equation then simplifies to

$$\frac{X^2}{.01} = 1.85 \times 10^{-5}$$

$$X^2 = 1.85 \times 10^{-7} = 18.5 \times 10^{-8}$$

$$X = 4.3 \times 10^{-4} \text{ mole per liter}$$

The concentration of the H^+ and Ac^- ions is then calculated to be 4.3×10^{-4} molar. We may now inspect the original equation to see if we were justified in neglecting X in the denominator expression of $.01 - X$. ($.01 - .000431 = .009569$.) This is almost equal to .01 and, for all practical purposes, the neglecting of X in the original expression was thus justified. If, however, X were so large that it could not be neglected (say 10 percent of the value from which it is subtracted or to which it is added) then the equation must be solved by the general solution of the quadratic equation (see the Appendix).

In a 0.1 molar solution of acetic acid the concentration of the H^+ ion is .00135 molar, while in a .01 molar solution we have just found it to be .000431 molar. The H^+ ion concentration is smaller in the more dilute solution. However, in the dilute solution a greater fraction of the total amount of acetic acid present is dissociated; 1.35 percent in the 0.1 molar solution and 4.3 percent in the .01 molar solution. We would be led to expect such a condition by a consideration of the processes taking place to maintain equilibrium. In the more dilute solutions the H^+ and Ac^- ions are farther apart and do not collide as often. Therefore a larger fraction of the molecules must remain in the dissociated state.

We can arrive at the same conclusion through an application of the Rule of Le Chatelier to this equilibrium (equation 4). Let us assume that we have a 0.1 molar solution in which, according to our calculations, 1.35 percent of the total amount of acetic acid is in the form of H^+ and Ac^- ions. These ions and the remaining undissociated acetic acid molecules are in equilibrium with each other. Now let us add some water to the solution to make it more dilute. This imposes a stress upon the equilibrium which in turn shifts in such a way as to undo its effect. The original 0.1 molar solution contained a definite number of H^+ and Ac^- ions but when water was added for dilution, temporarily the number of particles (ions plus molecules) per unit of volume became less than that originally present. To undo the effect of the stress (the dilution in this case) more acetic acid molecules dissociate to produce more

ions, and since by dissociation one molecule produces two ions the net effect is to increase the total number of particles. The reaction proceeds in such a way as partially to undo the effect of the dilution. The dissociation of the acetic acid does not continue until the concentration of the ions, expressed in moles per liter, is the same as in the original 0.1 molar solution, since equilibrium is reached before dissociation has proceeded to such an extent. The removal of water from the solution would produce an opposite effect; H^+ and Ac^- ions would combine to form acetic acid molecules. There would be a shift in the equilibrium to the left (equation 4).

The Common Ion Effect. From a consideration of the Rule of Le Chatelier we can predict that the effect of adding either H^+ or Ac^- ions to a solution of acetic acid will be to shift the equilibrium in such a way as to decrease the amount of acid dissociated, i.e., to increase the amount of undissociated acid. From the Law of Chemical Equilibrium, which in fact is a more concise and exact form of the Rule of Le Chatelier, it is possible to calculate the extent to which the equilibrium is shifted and to calculate the concentrations of the H^+ and Ac^- ions present when either of these ions has been added in some form other than acetic acid. For example, let us calculate the concentration of the H^+ ion in a 0.1 molar solution of acetic acid when 0.1 mole of NaAc, sodium acetate, has been added to 1 liter of this same solution. Sodium acetate is a salt, a strong electrolyte, and is completely dissociated in this solution as well as in a solution made by adding it to pure water. The equilibrium is the same as that for the previous example except that the concentrations of the substances involved will be different. Let X equal the number of moles of HAc per liter which has dissociated. (In this case X will not have the same value as it would for a solution containing only HAc at this concentration.) The concentration of the undissociated acid is then $0.1 - X$. The dissociation of X moles of HAc produces X moles of H^+ ions and X moles of Ac^- ions, but the concentration of the Ac^- ion is not the same as that of the H^+ ion. In this case it is $0.1 + X$, since the sodium acetate

supplies 0.1 mole of Ac^- ions per liter and the acetic acid supplies X moles per liter. The value of X, the H^+ ion concentration, may now be calculated.

$$\frac{(H^+)(Ac^-)}{(HAc)} = \frac{X(0.1 + X)}{(0.1 - X)} = 1.85 \times 10^{-5}$$

Again simplify the expression by considering X small as compared with 0.1. Then both $0.1 + X$ and $0.1 - X$ are practically equal to 0.1, and the equation becomes

$$\frac{(X)(0.1)}{(0.1)} = 1.85 \times 10^{-5}$$

or

$$X = 1.85 \times 10^{-5} \tag{7}$$

We see that X is small as compared with 0.1 and we were justified in neglecting it in those terms in which it was added to and subtracted from 0.1.

The H^+ ion concentration in the acetic acid solution containing sodium acetate was found to be 1.85×10^{-5} M. In the pure acetic acid solution the H^+ ion concentration was 1.35×10^{-3} M, about 75 times larger. The dissociation of the HAc molecules was repressed by the addition of the common ion.

In the same way we could calculate the concentration of the Ac^- ion in a HAc solution to which H^+ ion has been added (as HCl, for example) and again we would find that under these conditions fewer HAc molecules dissociate. In other words, the addition of H^+ ion shifts the equilibrium again to the left as shown in equation (4).

The Law of Chemical Equilibrium Does Not Apply to Strong Acids. Hydrochloric and nitric are typical examples of strong acids. These electrolytes, like the majority of the salts, we regard as 100 percent ionized in solution. On the basis of the concept of complete ionization, the Law of Chemical Equilibrium cannot be applied, for in such a case the concentration of the undissociated acid would be zero and the value of the equilibrium constant, infinity. In a .01 molar solution of hydrochloric acid, for example, the concentrations

of the H^+ and Cl^- ions are both .01 molar and that of the undissociated HCl molecules, zero.

$$\frac{(H^+)(Cl^-)}{(HCl)} = \frac{.01 \times .01}{0} = \text{infinity} * \qquad (8)$$

The Mass Law expression applies only to systems of substances in equilibrium, and if no undissociated molecules of HCl exist, there can be no equilibrium involving this substance. However, HCl molecules were once regarded as existing in dilute solutions. As we have previously shown, solutions of HCl have a greater equivalent conductance the more dilute the solution. The fact that the more concentrated solutions do not show as high an equivalent conductance as the dilute solutions was regarded as evidence that there are relatively fewer ions present in the more concentrated solutions; hence, undissociated molecules were believed to exist. In a previous chapter it was shown that this decrease of conductance in the more concentrated solutions was due rather to a "drag-effect."

Following the older views for the moment, we shall tentatively regard hydrochloric acid as only partially dissociated. From conductance data together with this assumption we can calculate the fractional number of apparently undissociated and dissociated HCl molecules as well as the values for the apparent "dissociation constant" of hydrochloric acid at different concentrations. Table 16 gives the apparent "dissociation constants" of hydrochloric acid so calculated.

Passing from 0.2 molar to .001 molar the value of the dissociation constant so calculated varies more than tenfold. The same trend in the value of the equilibrium constant with varying concentration is obtained in the case of all other strong electrolytes. If we now compare these values with those obtained for acetic acid, which obeys the Law of Mass Action, we note a striking difference in the behavior of the two acids (Table 17).

* Any finite number divided by *zero* equals infinity.

TABLE 16

APPARENT DISSOCIATION CONSTANTS OF HYDROCHLORIC ACID
(Assuming Incomplete Ionization)

Concentration (Moles per Liter)	$K = \frac{(H^+)(Cl^-)}{(HCl)}$
0.200	1.56
0.100	1.05
0.050	0.73
0.020	0.45
0.010	0.32
0.005	0.23
0.002	0.15
0.001	0.12

TABLE 17

DISSOCIATION CONSTANTS OF ACETIC ACID
(Experimentally Determined from Conductance Data)

Concentration (Moles per Liter)	$K = \frac{(H^+)(Ac^-)}{(HAc)}$
0.07369	0.0000185
0.03685	0.0000186
0.01842	0.0000185
0.00921	0.0000186
0.00461	0.0000186
0.00230	0.0000186
0.00115	0.0000186
0.00057	0.0000186

In the case of acetic acid the constant has the same value well within 1 percent for a large range of concentrations. The lack of conformity of the strong acids and other strong electrolytes to the Law of Chemical Equilibrium was one of the chief arguments for abandoning the theory of incomplete dissociation for these substances and for adopting, instead, the theory of complete dissociation for all strong electrolytes.

The Extent of Ionization of Weak Acids. Weak acids differ considerably in their ability to ionize; the weaker acid, by definition, has a smaller tendency to dissociate. The ionization constant of an acid is of course a quantitative measure of this tendency. An acid with a very small constant has a small tendency to ionize while one with a relatively large constant ionizes to a larger extent. The following table shows a few typical weak acids together with their ionization constants at room temperature, and the percent of ionization of their 0.1 molar aqueous solutions.

TABLE 18

TYPICAL WEAK ACIDS, THEIR IONIZATION CONSTANTS AND EXTENT OF IONIZATION

Acid	Percent Ionization of 0.1 Molar Solution	K (Ionization Constant)
Dichloracetic	52	5.5×10^{-2}
Salicylic	10	1.1×10^{-3}
Nitrous	6.5	4.5×10^{-4}
Acetic	1.36	1.85×10^{-5}
Hydrocyanic	0.0065	4.0×10^{-10}
Phenol	0.003	1.0×10^{-10}

The extreme variation among weak acids in the ability to ionize is well illustrated by this table; the extent of ionization of their 0.1 molar solutions varies from 52 percent for dichloracetic acid to .003 percent for phenol (carbolic acid).

The question which naturally arises is: When is an acid to be regarded as a weak acid and when a strong acid? Arbitrarily, we may answer this question in a simple way. An acid may be regarded as belonging to the weak class if its dilute solutions obey the Law of Mass Action. Such acids as hydrochloric, sulfuric and nitric are without question to be regarded as strong acids (100 percent ionized). When we search further for the reason that some acids are weak and some are strong, we find ourselves inquiring into the electronic

structures or make-up of the molecules in question. The problem is a very complicated one which involves not only the tendencies of the different molecules to hold fast their dissociable hydrogen ions but also the tendency of surrounding water molecules to hold the dissociation products (hydrogen ions and negative ions) and thus aid the dissociation process. As we have pointed out before ions in solution do not exist independently in the condition indicated by their formulae but are surrounded by and attached, more or less firmly, to water molecules.

All Substances in the Same Solution Must Be in Equilibrium. When two or more weak acids, or in fact any weak electrolytes, are present in the same solution, they must all be in equilibrium with their respective ions. For example, if a solution contains both acetic and hydrocyanic acids, the following equilibria must be maintained:

$$HAc = H^+ + Ac^- \tag{9}$$

$$HCN = H^+ + CN^- \tag{10}$$

In this case the hydrogen ion is common to the two equilibria and since it exists in the same solution it must have only one concentration. The acetic acid ionizes to a larger extent than the hydrocyanic acid and produces more hydrogen ions, but this excess concentration of hydrogen ion represses the ionization of hydrocyanic acid and in this solution the latter is ionized to a smaller extent than it is when it exists alone in water solution. But the hydrocyanic acid also ionizes to a small extent to produce some hydrogen ions. For this reason the acetic acid is likewise ionized to a slightly smaller extent than it is in pure water. The common hydrogen ion represses the ionization of both acids in such a mixed solution. The calculation of the concentration of the hydrogen ion in a mixed solution (0.1 molar with respect to both acetic acid and hydrocyanic acid) becomes slightly more complicated than the simpler case of one acid, due to the necessity of solving simultaneous equations.

Some acids dissociate in two or more steps. Carbonic acid,

H_2CO_3, is an example of this type. The first step of the dissociation of this acid results in the formation of the bicarbonate ion, HCO_3^-, and H^+ ion in accordance with the equation

$$H_2CO_3 = H^+ + HCO_3^- \qquad (11)$$

The second step consists of the dissociation of the bicarbonate ion:

$$HCO_3^- = H^+ + CO_3^{--} \qquad (12)$$

In any solution containing carbonic acid, both these acids (H_2CO_3 and HCO_3^-) are present and, like a mixed solution of acids, they are in complete equilibrium with each other and their common hydrogen ion. A fuller treatment of such acids will be considered in Chapter 9.

Weak Bases. Equilibria involving weak bases may be treated in the same manner as was done above in the case of weak acids with the exception, of course, that the bases dissociate to give hydroxide ions, OH^-, in solution.

TABLE 19

IONIZATION CONSTANTS OF SOME WEAK BASES

Base	Percent Ionization in 0.1 Molar Solution	K (Ionization Constant)
Methyl ammonium hydroxide	7.0	5.0×10^{-4}
Ammonium hydroxide	1.3	1.8×10^{-5}
Hydrazine hydroxide	0.003	9.8×10^{-7}
Phenyl ammonium hydroxide	0.0007	4.6×10^{-10}

The number of common weak bases is far smaller than that of the weak acids. The most common weak base is ammonium hydroxide, NH_4OH. This base is about as weak a base as acetic acid is a weak acid; the ionization constants are practically the same for the two substances. A few examples of weak bases appear in the table above; others together with their ionization constants are listed in the Appendix.

Just as ammonium hydroxide is known only in solution and

not in the pure state, so methyl ammonium hydroxide and phenyl ammonium hydroxide are known only in solution. In the pure state these substances are known as methyl amine, CH_3NH_2, and phenyl amine, $C_6H_5NH_2$ (aniline), respectively. They are the analogues of ammonia with one hydrogen atom replaced by a methyl or phenyl group, and like ammonia, NH_3, they take up water in solution to form the hydroxide.

Indicators. Certain natural and synthetic colored substances have the property of either changing color or becoming colorless in dilute solution when the hydrogen ion concentration in the solution attains a definite and fixed value. Phenolphthalein, for example, is a colorless substance in any solution for which the hydrogen ion concentration is greater than 10^{-9} mole per liter. In solutions for which the hydrogen ion concentration is less than this value the phenolphthalein imparts a red or pink color to the solution. Methyl violet in solution is green when the hydrogen ion concentration is greater than 10^{-2} mole per liter, blue for hydrogen ion concentrations of 10^{-3} to 10^{-2} mole per liter and violet for solutions for which the hydrogen ion concentration is less than 10^{-3} mole per liter. A great number of such substances are known and enough can be selected so that the hydrogen ion concentration can be determined somewhat roughly over a wide range of concentration. The table of indicators on page 137 gives such a series, together with their colors for corresponding hydrogen ion concentrations.*

Litmus, one of the first known of the indicators, changes from blue to red when the hydrogen ion concentration becomes greater than 10^{-8} molar. The change is so gradual that it is not entirely red until the solution has a hydrogen ion concentration greater than 10^{-5} molar. Accordingly, litmus is a poor indicator for determining the hydrogen ion concentration of a solution.

* In all water solutions there is a definite relationship between the hydrogen ion and hydroxide ion concentrations. This relationship, which becomes evident from a study of the first two rows of the table, is treated fully in Chapter 10 on hydrolysis.

TABLE 20

INDICATORS

H^+ Conc.	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
OH^- Conc.	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
*p*H	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

Methyl violet	yellow	green blue	blue ←						violet →						
Methyl orange	red →				orange ←				yellow →						
Methyl red	—	red →			←				yellow →						
Brom cresol purple	yellow →							←	purple →						
Brom thymol blue	yellow →						green ←					blue →			
Phenol-phthalein	colorless →									←		red →			
Thymol blue	red →	←		yellow →						←		blue →			
Thymol-phthalein	←		colorless →								←	blue →			
Tri-nitro benzene	←		colorless →										orange	red orange	

In determining the hydrogen ion concentration of any solution, a number of indicators must be used and by a process of elimination the hydrogen ion concentration can be fixed within rather narrow limits. For finer work the color of the indicator in the unknown solution should be compared with its color in some solution for which the hydrogen ion concentration is known. Such solutions can be made by mixing known quantities of acids and their salts for which the hydrogen ion concentrations have been determined by other methods. The usual method of originally determining the hydrogen ion concentration of a standard solution employs the hydrogen electrode. This method cannot be discussed in this course. It is usually treated more fully in courses in quantitative analysis and in physical chemistry.

Indicators are generally considered as weak acids or weak bases, with the color of the indicator ion different from that of the undissociated compound. The general equation for the dissociation of an indicator acting as an acid is

$$\text{Ind} = \text{Ind}^- + \text{H}^+ \tag{13}$$

With methyl orange, for example, the unionized acid (Ind) is red and the ion (Ind^-) is yellow. The dissociation constant for this indicator is equal to 2×10^{-4}.

$$\frac{(\text{Ind}^-)(\text{H}^+)}{(\text{Ind})} = K_{\text{Ind}} = 2 \times 10^{-4} \tag{14}$$

When the undissociated acid form and the ion form of the indicator are present in equal amounts ($\text{Ind} = \text{Ind}^-$), it is apparent that the H^+ concentration equals the K_{Ind}.

pH Values. For convenience the hydrogen ion concentration is often expressed in terms of *p*H values. The *p*H value of a solution is defined as the logarithm of the reciprocal of the hydrogen ion concentration. In other words,

$$p\text{H} = \log \frac{1}{(\text{H}^+)} \tag{15}$$

The *p*H value of a solution for which the hydrogen ion concentration is 10^{-4} *M*, for example, is 4; the *p*H for a solution

whose hydrogen ion concentration is 10^{-9} M is 9, etc. For a fuller treatment of this quantity the student is referred to the paragraphs on exponential numbers, logarithms and pH values in the Appendix.

pK Values. Just as it is often convenient to express the hydrogen ion concentration by pH values, it may also be desirable in some cases to express equilibrium constants by pK values. The pK for any equilibrium is defined as the logarithm, to the base 10, of the reciprocal of the equilibrium constant.

$$p\mathrm{K} = \log \frac{1}{K_{eq}} \tag{16}$$

Since

$$\log \frac{1}{K_{eq}} = -\log K_{eq}$$

$$p\mathrm{K} = -\log K_{eq}$$

Thus, for example, the pK for the equilibrium

$$\mathrm{HAc} = \mathrm{H^+} + \mathrm{Ac^-}$$

is equal to $-\log K_1$. The equilibrium constant for this reaction is equal to 1.85×10^{-5}. Therefore $\log K_1 = \log 1.85 + \log 10^{-5} = 0.27 - 5 = -4.73$; $p\mathrm{K} = -(-4.73) = 4.73$.

The equilibrium constants given in the tables in the Appendix following the text are expressed in two ways. In the last column the value of the constant is given as a purely exponential number. The pK is the negative value of the exponent of this exponential number. The equilibrium constant for HCN, for example, is $10^{-9.4}$. The pK value for HCN is therefore 9.4.

Any equilibrium constant can be expressed in this manner.

The Brønsted Definitions of Acids and Bases. In the Brønsted system, acids and bases are defined in broader and more general terms than was commonly done in the past. The older established definitions restricted an acid to a substance producing hydrogen ions, and a base to a substance producing hydroxide ions in water solution. But it is well recognized that many substances other than hydroxides behave like bases in that they produce basic solutions and react with acids;

sodium carbonate for example. Furthermore, when solvents other than water are taken into consideration the number of substances which act like hydroxides in water solution increases greatly. The Brønsted definitions are so general that they include as bases all substances which combine with hydrogen ions not only in water solution but in all solvents. The definition of an acid is not greatly different from that previously used.

An acid is defined as any substance in ionic or molecular form, which produces or donates protons (H^+), *while a base is any substance which accepts or acquires protons.* We shall consider these definitions from the standpoint of the equilibrium existing between the proton donor and the proton acceptor, i.e., between the acid and the base. Since the equilibrium reactions are reversible neither an acid nor a base is considered separately; when an acid dissociates or transfers protons it produces a base and when a base accepts protons an acid is formed. This perhaps may be better expressed by the equation

$$\text{Acid} = H^+ + \text{Base} \tag{17}$$

The acid produces protons (left to right) and the base acquires protons (right to left).

Since our consideration of acids and bases is to be restricted very largely to water solutions, let us consider the equilibrium existing between the proton, water, and the hydronium ion. This relationship is expressed by the equation

$$H_3O^+ = H^+ + H_2O \tag{18}$$

Here H_3O^+, hydronium ion, is the acid (proton donor) and H_2O is the base (proton acceptor). This equilibrium is considered as being very largely in favor of H_3O^+, i.e., the concentration of free protons is very small; almost all of them are attached to water molecules. Accordingly, the hydrogen ion in solution is symbolized by H_3O^+ and not by H^+. In the older established definitions all forms of the hydrogen ion, H^+, H_3O^+ and higher hydrates are represented as a group by the symbol H^+ and the equilibrium as expressed in equation (18)

is never considered explicitly because it is recognized that the protons exist very largely in the hydrated form.

According to these definitions the ammonium ion is an acid.

$$NH_4^+ = H^+ + NH_3 \tag{19}$$

In this case ammonia, NH_3, is the base. However, if this reaction takes place in water solution the protons formed attach themselves to water molecules to form hydronium ions and the complete reaction is

$$\underset{\text{Acid}_1}{NH_4^+} + \underset{\text{Base}_2}{H_2O} = \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{NH_3} \tag{20}$$

In effect the proton is merely transferred from the NH_4^+ ion to the water molecule and *vice versa*. The NH_4^+ and the H_3O^+ ions are acids and H_2O and NH_3 are bases. The process is that of neutralization, with the salt formation not emphasized by the equation representing it. In this reaction, the two bases NH_3 and H_2O are competing for protons, with the NH_3 having the greater tendency to acquire them.

Water itself may act as an acid as well as a base.

$$H_2O = H^+ + OH^- \tag{21}$$

In this case water is the acid molecule and the OH^- ion is the base. Again, this does not represent the complete reaction for according to reaction (18) the protons combine with water molecules. The reaction is rather represented by the equation

$$\underset{\text{Acid}_1}{H_2O} + \underset{\text{Base}_2}{H_2O} = \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{OH^-} \tag{22}$$

In the complete reaction water acts both as an acid and as a base. It should be borne in mind that the OH^- ion is also hydrated but this hydration is not expressed in the formula. Hydration or combination with water is only expressed in the formulae for the hydrogen ion and for amphoteric substances some of which will be considered in a later chapter.

The fact that HCl in the pure state is virtually a nonconductor while its water solution shows a high conductivity is not as easily expressed in terms of the established definitions

as it is with the newer definitions. Pure HCl, a liquid with a boiling point of −83° C., dissociates into protons and chloride ions. The equation for this equilibrium is

$$HCl = H^+ + Cl^- \tag{23}$$

Both the proton and the chloride ion are probably "solvated," i.e., joined to HCl molecules. In fact we might reason by analogy that the formula of the hydrogen ion is really H_2Cl^+. On the basis of the Brønsted definitions we then can write the reaction as

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{HCl} = \underset{\text{Acid}_2}{H_2Cl^+} + \underset{\text{Base}_1}{Cl^-} \tag{24}$$

The reaction which takes place when pure HCl is added to water may be represented by

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} = \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Cl^-} \tag{25}$$

In this case the hydrogen ion is present as H_3O^+ while in pure HCl it is present as H_2Cl^+. The Cl^- ions are also different in the two cases but the difference is not indicated in the formula. It is apparent that HCl in the pure state and HCl in water solution are different but there is no *a priori* reason based on these definitions alone which tells us that the conductivity is very low in pure HCl, i.e., that the equilibrium in equation (24) lies largely in the direction of undissociated HCl, while in water it lies in the direction of the dissociated form (to the right in equation 25). By the older definitions both cases are represented by equation (23); the difference between the two cases is implied and left more to the imagination or to the visualization of the experimental conditions.

Systems such as those expressed by equation (25) are known as conjugated acid-base systems. $Base_1$ is the base of $Acid_1$ and $Base_2$ is the base of $Acid_2$. A weak acid such as HAc in water solution, as indicated in the following equation, is also a part of a conjugated acid-base equilibrium system.

$$\underset{\text{Acid}_1}{HAc} + \underset{\text{Base}_2}{H_2O} = \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Ac^-} \tag{26}$$

The new base indicated here is the Ac^- ion. It conforms in its properties with the definition of a base, that is, it shows a tendency to combine with the proton to produce the HAc molecule.

An acid which has a great tendency to donate protons is known as a strong acid while a base which has a great tendency to accept protons is a strong base. Acetate ion is a strong base and acetic acid is therefore a weak acid. Chloride ion in water solution is a very weak base; in fact it is so weak that in dilute solution it is no base at all, and therefore HCl in water solution is a very strong acid. In pure HCl, however, chloride ion is a strong base and HCl is a weak acid.

The ionization of a number of acids in water solution may be represented by the following equations. The order is given in decreasing strength of the acid.

$Acid_1$		$Base_2$		$Acid_2$		$Base_1$	
HSO_4^-	+	H_2O	=	H_3O^+	+	SO_4^{--}	(27)
H_3PO_4	+	H_2O	=	H_3O^+	+	$H_2PO_4^-$	(28)
HNO_2	+	H_2O	=	H_3O^+	+	NO_2^-	(29)
$HCNO$	+	H_2O	=	H_3O^+	+	CNO^-	(30)
H_2CO_3	+	H_2O	=	H_3O^+	+	HCO_3^-	(31)
H_2S	+	H_2O	=	H_3O^+	+	HS^-	(32)
$H_2PO_4^-$	+	H_2O	=	H_3O^+	+	HPO_4^{--}	(33)
HCN	+	H_2O	=	H_3O^+	+	CN^-	(34)
HCO_3^-	+	H_2O	=	H_3O^+	+	CO_3^{--}	(35)
HPO_4^{--}	+	H_2O	=	H_3O^+	+	PO_4^{---}	(36)
HS^-	+	H_2O	=	H_3O^+	+	S^{--}	(37)

For strong acids, all of which are practically completely ionized in water solution, the following examples are cited.

$Acid_1$		$Base_2$		$Acid_2$		$Base_1$	
H_2SO_4	+	H_2O	=	H_3O^+	+	HSO_4^-	(38)
HNO_3	+	H_2O	=	H_3O^+	+	NO_3^-	(39)
HCl	+	H_2O	=	H_3O^+	+	Cl^-	(40)

All of the anions designated as $Base_1$ are to be regarded as bases. These are merely representative of a much larger number of anions which behave as bases in that they all show

a tendency to acquire the proton. Of this group of anions, the HSO_4^-, NO_3^-, and Cl^- ions certainly show little if any tendency to acquire the proton. According to the older definitions we have already classified the corresponding acids, H_2SO_4, HNO_3, and HCl as strong and 100 percent ionized. How then can the anions of these acids be called bases? In water solution these acids are practically completely ionized, but in the pure state as liquids these acids show very little ionization. If we consider the reaction of Cl^- ion with the hydronium ion to form HCl gas or liquid, then there is some justification for calling the Cl^- ion a base.

Returning to equation (26), we may write the equilibrium expression as

$$\frac{(H_3O^+)(Ac^-)}{(HAc)(H_2O)} = K_{eq}^{B} \tag{41}$$

The concentration of the water in the denominator remains practically constant during the course of any reaction since the water is either produced or consumed in amounts which are negligible compared to the total amount of water present. We may consider this value as constant and include it in the value for the equilibrium constant. It is therefore omitted from the expression which may now be written.

$$\frac{(H_3O^+)(Ac^-)}{(HAc)} = K_1 = 1.85 \times 10^{-5} \tag{42}$$

The symbol for the hydronium ion, H_3O^+, is merely a symbol for expressing the same particle in solution as is denoted by the simpler symbol, H^+. We may use any symbols we choose for designating particles in solution, but it is evident that the value for the equilibrium constant is independent of our method of naming the particles participating in the equilibrium. Accordingly, K_1^B of equation (42) has the same value as that given in the older established system, namely, 1.85×10^{-5}.

On the basis of the older definitions we have termed NH_4OH a weak base since it ionizes only slightly to produce NH_4^+ and OH^- ions. The equilibrium in solution is one which involves all three particles, the NH_4^+ and OH^- ions, and NH_4OH mole-

cules. When NH_3 gas is passed into water the following equilibria are considered.

$$NH_3 + H_2O = NH_4OH = NH_4^+ + OH^- \qquad (43)$$

Whether NH_4OH molecules actually exist in solution we do not know, and as a matter of fact it makes no difference whether we consider the solution as one composed of NH_3 molecules, NH_4OH molecules, or both, since the equilibria are independent of our method of naming the particles.

Suppose we omit the intermediate NH_4OH molecule from our equation. We then have

$$\underset{\text{Base}_1}{NH_3} + \underset{\text{Acid}_2}{H_2O} = \underset{\text{Acid}_1}{NH_4^+} + \underset{\text{Base}_2}{OH^-} \qquad (44)$$

In applying our definitions of acids and bases, we see the NH_3 is a base since it combines with the proton to give NH_4^+ ion. This reaction can be considered as taking place in two steps, as can the other similar foregoing reactions.

$$H_2O = H^+ + OH^- \qquad (45)$$

and

$$NH_3 + H^+ = NH_4^+ \qquad (46)$$

The H_2O gives up H^+ ions which are then taken up by the NH_3 molecules. By adding equations (45) and (46), equation (44) is obtained.

The equilibrium expression for equation (44) is

$$\frac{(NH_4^+)(OH^-)}{(NH_3)} = K_{eq}{}^{B} = 1.8 \times 10^{-5} \qquad (47)$$

This expression is the same as we obtain when the ammonia in water is considered to be ammonium hydroxide, NH_4OH. The two substances, NH_3 and NH_4OH, are one and the same; different symbols are used to designate them.

In equation (44) the reaction is one in which the two bases NH_3 and OH^- ion are competing with each other for the proton. At equilibrium the reaction will predominate either to the left or to the right depending upon whether the OH^- ion or the NH_3 molecule is the stronger base, that is, whether the OH^- ion or the ammonia molecule holds the proton more firmly.

On the basis of the proton transfer concept of acids and bases, it is apparent that the term "salt" is of little significance, since the ions of most salts may be considered either as acids or bases. These ions will either lose protons or acquire protons, and these two processes are all that is essential to conform to the definitions of acids and bases. Practically all negative ions may be considered as bases since they combine with protons. Many positive ions are acids in that they will give up protons but, on the other hand, most positive ions do not show this tendency to any marked degree. If a metallic ion is to be regarded as an acid it is apparent that its formula must include protons which it can donate. Therefore for this purpose the symbol for the hydrated form of the ion is used. Such cases will be presented later.

In the following chapters of this text we shall retain the established definitions of acids and bases, except in those sections in which we deal explicitly with the Brønsted definitions.

Examples of Problems

Example 1.

Calculate the (H^+) in a 0.1 molar HCNO solution. What is the degree of ionization of cyanic acid in this same solution? $K_1 = 2 \times 10^{-4}$.

$$HCNO = H^+ + CNO^-$$

The concentration (0.1 molar) given for HCNO is that for the total HCNO, in solution, both dissociated and undissociated.

Let $$(H^+) = X$$

(CNO^-) must also be X in this case, for as many CNO^- as H^+ ions are formed by the dissociation process.

$$(HCNO) = 0.1 - X$$

Substituting these values in the equilibrium expression, we have

$$\frac{(H^+)(CNO^-)}{(HCNO)} = \frac{X^2}{0.1 - X} = 2 \times 10^{-4}$$

By inspection of this equation we see that X is relatively small as compared with 0.1, therefore for all practical purposes

$$0.1 - X \approx 0.1$$

Then

$$\frac{X^2}{0.1 - X} = \frac{X^2}{0.1} = 2 \times 10^{-4}$$

$$X^2 = 2 \times 10^{-5} = 20 \times 10^{-6}$$

$$X = 4.5 \times 10^{-3}$$

X = .0045 mole per liter = (H^+) = (CNO^-)

From the value of X so obtained we can readily see that we were justified in neglecting X as compared with 0.1, for $0.1 - .0045 = .0955$, which is near enough to 0.1 that, for the purpose of our expected accuracy, it may be neglected. If we solve the equation

$$\frac{X^2}{0.1 - X} = 2 \times 10^{-4}$$

by the use of the quadratic solution (see Appendix), we obtain a value for X of .0044 mole per liter. This again shows the justification for the simple solution.

The degree of ionization is the fractional number of molecules dissociated, or the amount per liter of the dissociated weak electrolyte divided by the total concentration (both dissociated and undissociated). Since, in this particular example, the concentration of H^+ and CNO^- is 4.5×10^{-3} mole per liter, the amount of the dissociated HCNO has this same value, for 4.5×10^{-3} mole of HCNO gives 4.5×10^{-3} mole of H^+ and 4.5×10^{-3} mole of CNO^- upon dissociation.

$$\text{Degree of dissociation} = \frac{4.5 \times 10^{-3}}{0.1} = 4.5 \times 10^{-2} \text{ or } 4.5 \text{ percent.}$$

Example 2

In a 0.1 molar solution of a hypothetical acid, HA, the degree of dissociation is .025. Calculate the ionization constant for the acid HA.

$$HA = H^+ + A^-$$

$$.025 = \frac{\text{Concentration of dissociated HA}}{\text{Total HA}}$$

$$= \frac{(H^+)}{0.1}$$

$$(H^+) = 0.1 \times .025 = .0025 = (A^-)$$

$$\text{The ionization constant} = \frac{(H^+)(A^-)}{(HA)}$$

$$= \frac{2.5 \times 10^{-3} \times 2.5 \times 10^{-3}}{.0975}$$

$$K_I = 6.4 \times 10^{-5}$$

Example 3.

(a) What is the concentration of the H^+ in a solution containing 0.1 mole per liter HCNO and 0.1 mole NaCNO per liter?

$$HCNO = H^+ + CNO^-$$

NaCNO is completely ionized, so it contributes 0.1 mole CNO^- per liter. Let X equal the number of moles per liter of HCNO dissociated, which also equals (H^+). (CNO^-) will be $0.1 + X$ and the (HCNO) undissociated, $0.1 - X$.

$$K_I = 2 \times 10^{-4} = \frac{(H^+)(CNO^-)}{(HCNO)}$$

$$= \frac{X(0.1 + X)}{(0.1 - X)}$$

Neglecting X in comparison with 0.1, we have

$$(0.1 + X) \approx 0.1$$
$$(0.1 - X) \approx 0.1$$

Then $$\frac{X(0.1)}{0.1} = 2 \times 10^{-4}$$

$$X = 2 \times 10^{-4} \text{ mole per liter} = (H^+)$$

(b) What is the degree of ionization of the HCNO in this solution?

The degree of ionization is the fractional number of molecules ionized. This is equivalent to the concentration of the hydrogen ion divided by the total concentration of HCNO present, both in the form of ions and unionized molecules.

$$\text{Degree of ionization} = \frac{(H^+)}{0.1} = \frac{2 \times 10^{-4}}{0.1} = .002$$

The percent of ionization = $.002 \times 100 = 0.2$.

Thus, 0.2 percent of the HCNO is present in solution as H^+ and CNO^- ions.

Example 4.

If 100 ml. of 0.1 *M* NH_4Cl solution are added to 150 ml. of 0.1 *M* NH_4OH solution, what is the OH^- ion concentration in the resulting solution? $K_I(NH_4OH) = 1.8 \times 10^{-5}$.

The concentration of the NH_4^+ ion is the same as it would be if the 100 ml. of 0.1 *M* NH_4Cl solution were diluted to 250 ml. by adding water, so the (NH_4^+) from the $NH_4Cl = 0.1 \times \frac{100}{250} = .04$ *M*.

The concentration of the NH_4OH is the same as it would be if

the 150 ml. of 0.1 *M* NH_4OH solution were diluted to 250 ml. by water, so the total NH_4OH concentration is $0.1 \times \frac{150}{250} = .06$ *M*.

Substances in solution:	NH_4OH	=	NH_4^+	+	OH^-
Concentrations:	$.06 - X$		$.04 + X$		X

$$\frac{(NH_4^+)(OH^-)}{(NH_4OH)} = \frac{(.04 + X)X}{(.06 - X)} = 1.8 \times 10^{-5}$$

Neglecting X as compared with .04 and .06,

$$\frac{(.04)X}{(.06)} = 1.8 \times 10^{-5}$$

$$X = \frac{.06}{.04} \times 1.8 \times 10^{-5} = 2.7 \times 10^{-5}\ M$$

$$\text{i.e., } (OH^-) = 2.7 \times 10^{-5}\ M$$

Example 5.

If 0.1 mole solid NaOH is added to 1 liter of 0.125 *M* HAc solution, what is the final H^+ concentration? (Assume no volume change.)

0.1 mole NaOH neutralizes 0.1 mole HAc to form 0.1 mole NaAc and leaves .025 mole HAc not neutralized in the one liter. The solution now is 0.1 *M* with respect to NaAc and .025 *M* with respect to HAc.

Substances in solution:	HAc	=	H^+	+	Ac^-
Concentrations:	$.025 - X$		X		$0.1 + X$

$$\frac{(H^+)(Ac^-)}{(HAc)} = \frac{X(0.1 + X)}{(.025 - X)} = 1.85 \times 10^{-5}$$

Neglecting X as compared with 0.1 and with .025,

$$\frac{X(0.1)}{(.025)} = 1.85 \times 10^{-5}$$

$$X = \frac{(.025)}{(0.1)} \times 1.85 \times 10^{-5}$$

$$X = 0.46 \times 10^{-5} = 4.6 \times 10^{-6}\ M \qquad \text{i.e., } (H^+) = 4.6 \times 10^{-6}\ M$$

Example 6.

100 ml. of 0.1 *M* NaOH is added to 150 ml. 0.2 *M* HAc. Calculate the final H^+ concentration.

Before reaction, 100 ml. 0.1 *M* NaOH contains .01 mole NaOH.

Before reaction, 150 ml. 0.2 *M* HAc contains .03 mole HAc.

.01 mole NaOH neutralizes .01 mole HAc, producing .01 mole NaAc in solution and leaving .02 mole HAc not neutralized.

After reaction, the .01 mole NaAc and .02 mole HAc are contained in 250 ml. solution, so the concentrations are .04 M and .08 M respectively.

Substances in solution:	HAc	=	H^+	+	Ac^-
Concentrations:	$.08 - X$		X		$.04 + X$

$$\frac{(H^+)(Ac^-)}{(HAc)} = \frac{X(.04 + X)}{(.08 - X)} = 1.85 \times 10^{-5}$$

Neglecting the X's in the terms $(.04 + X)$ and $(.08 - X)$,

$$\frac{X(.04)}{(.08)} = 1.85 \times 10^{-5}$$

$$X = \frac{(.08)}{(.04)} \times 1.85 \times 10^{-5}$$

$$X = (H^+) = 3.7 \times 10^{-5}\ M$$

Example 7.

Calculate the pH for a .01 M HCN solution.

$$K_{(HCN)} = 4 \times 10^{-10}$$

First calculate the (H^+).

Substances in solution:	HCN	=	H^+	+	CN^-
Concentrations:	$.01 - X$		X		X

$$\frac{(H^+)(CN^-)}{(HCN)} = \frac{X^2}{.01 - X} = 4 \times 10^{-10}$$

Neglecting X in the denominator,

$$\frac{X^2}{.01} = 4 \times 10^{-10}$$

$$X^2 = 4 \times 10^{-12}$$

$$X = 2 \times 10^{-6}\ M = (H^+)$$

$$p\text{H} = \log \frac{1}{(H^+)} = -\log (H^+)$$

$$\log (H^+) = \log (2.0 \times 10^{-6}) = \log 2.0 + \log 10^{-6}$$

$$\log 2.0 = 0.3$$

$$\log 10^{-6} = -6$$

$$\log (H^+) = \log (2.0 \times 10^{-6}) = 0.3 - 6 = -5.7$$

$$p\text{H} = -\log (H^+) = -(-5.7) = 5.7$$

(See also mathematical operations in the Appendix.)

Example 8.

The *p*H of a solution is 6.38. What is the concentration of the hydrogen ion in this solution?

$$p\text{H} = -\log (\text{H}^+) = 6.38 = -(-6.38)$$
$$\log (\text{H}^+) = -6.38 = -6.00 + (-0.38)$$
$$\log (\text{H}^+) = -7.00 + 0.62$$
$$\text{antilog of } -7 = 10^{-7}$$
$$\text{antilog } 0.62 = 4.17$$
$$(\text{H}^+) = 4.17 \times 10^{-7}\ M$$

Example 9.

What is the concentration of a HCN solution which is 0.2 percent ionized?

$$\text{HCN} = \text{H}^+ + \text{CN}^-$$

Let α = the degree of ionization = $\dfrac{(\text{H}^+)}{C}$, where C is the total HCN concentration. Therefore

$$(\text{H}^+) = C \times \alpha$$
$$(\text{CN}^-) = (\text{H}^+) = C \times \alpha$$
$$(\text{HCN}) = C(1 - \alpha)$$
$$\frac{(\text{H}^+)(\text{CN}^-)}{(\text{HCN})} = K_\text{I} = 4 \times 10^{-10}$$
$$\frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = 4 \times 10^{-10}$$
$$\frac{C \times (.002)^2}{1 - .002} = \frac{C \times 4 \times 10^{-6}}{0.998} = 4 \times 10^{-10}$$
$$C = \frac{4 \times 10^{-10} \times 0.998}{4 \times 10^{-6}} = 10^{-4}\ M\ \text{HCN}$$

Example 10.

A 0.2 *M* HCN solution is found to have a (H^+) of 1×10^{-6} *M*. Calculate the (CN^-) necessary to maintain this (H^+).

$$\text{HCN} = \text{H}^+ + \text{CN}^-$$
$$\frac{(\text{H}^+)(\text{CN}^-)}{(\text{HCN})} = K_\text{I} = 4 \times 10^{-10}$$

At equilibrium, the (HCN) has a value of $0.2 - .000001$ or 0.2 *M*, while the (H^+) is maintained at 1×10^{-6} *M*. Then

$$\frac{(H^+)(CN^-)}{(HCN)} = \frac{1 \times 10^{-6}(CN^-)}{0.2} = 4 \times 10^{-10}$$

$$(CN^-) = \frac{0.2 \times 4 \times 10^{-10}}{1 \times 10^{-6}} = 8 \times 10^{-5}\ M$$

Questions and Problems *

1. Will 0.1 mole of a weak acid in solution require more, less or the same amount of sodium hydroxide solution to neutralize it as 0.1 mole of a strong acid? Explain.
2. Is the percentage of molecules of HAc which are dissociated in a .001 *M* solution smaller, greater or the same as in a .01 *M* solution?
3. Considering HAc and its ions to be in a state of equilibrium,

   $$HAc = H^+ + Ac^-$$

   how can this equilibrium be shifted to the left and how to the right?
4. How does the application of the Law of Mass Action help support the theory of complete dissociation of strong electrolytes?
5. Which two indicators would you use to show that the hydrogen ion concentration in a given solution is less than 10^{-4} molar but greater than 10^{-7} molar?
6. Rewrite equations (1), (2), (3), (6), (9), (10), (11), and (12) of this chapter in terms of the Brønsted definitions.
7. What *p*H values correspond to the following H^+ ion concentrations:

   (a) 10^{-5} (b) 10^{-9} (c) 10^{-1} (d) $10^{-7.38}$ (e) $10^{-2.1}$
8. What is the concentration of the H^+ ion in moles per liter in each of the following solutions?

   (a) 0.1 *M* CH_3COOH (HAc)
   (b) 0.01 *M* CH_3COOH (HAc)
   (c) 1 *M* CH_3COOH (HAc)
   (d) 0.05 *M* HCN
   (e) 0.01 *M* HNO_2
   (f) 0.02 *M* HCNO
   (g) 0.001 *M* HN_3
   (h) 0.08 *M* $ClCH_2COOH$
   (i) 0.004 *M* HCN
   (j) 0.0001 *M* C_6H_5COOH

   Use quadratic equation for (e) and (j) (see Appendix).
9. Calculate the concentration of the OH^- ion in solutions of the following:

* Values for dissociation constants are given in the Appendix.

(a) 1 M NH_4OH
(b) 0.1 M NH_4OH
(c) 0.01 M NH_4OH
(d) 0.001 M NH_4OH
(e) 0.04 M NH_4OH
(f) 0.01 M CH_3NH_3OH
(g) 0.2 M $(CH_3)_2NH_2OH$
(h) 0.1 M $C_2H_5NH_3OH$
(i) 0.002 M $C_6H_5NH_3OH$

10. Solutions of the following weak acids and bases are ionized as indicated. Calculate the ionization constant in each case.

Solution	Percent Ionized
(a) 0.1 M CH_3COOH (HAc)	1.35
(b) 0.01 M CH_3COOH	4.20
(c) 0.1 M NH_4OH	1.33
(d) 0.01 M NH_4OH	4.15
(e) 0.1 M HNO_2	6.5
(f) 0.1 M HCN	0.0065
(g) 0.005 M HCN	0.029

11. Two grams of HAc are dissolved in 1 liter of water. Calculate the concentration of the H^+ ion and the Ac^- ion.

12. To the above solution (problem 11) 2 g. of NaAc are added. Now what is the concentration of the H^+ and Ac^- ions?

13. Calculate the degree of ionization of the solutes in the following aqueous solutions:

(a) 0.1 M HNO_2
(b) 0.01 M HCN
(c) 0.05 M HAc
(d) 0.02 M NH_4OH
(e) 0.08 M CH_3NH_3OH

14. If the H^+ concentration of a solution which contains 0.1 mole of HAc and a certain amount of NaAc per liter is .000025 M, what must be the concentration of the Ac^- ion?

15. It is desired to make the concentration of the H^+ ion 3.5×10^{-8} M in a .05 M solution of HCN. This can be accomplished by the addition of KCN. What must be the concentration of the CN^- ion in such a solution?

16. A 0.1 M solution of NH_4OH, also containing some NH_4Cl, is found to have an OH^- ion concentration of 0.25×10^{-5} M. What is the concentration of the NH_4^+ ion in this solution?

17. How many moles of NH_4Cl must be added to 1 liter of a 0.1 M solution of NH_4OH to make the OH^- ion concentration 1×10^{-5} M per liter?

18. If .01 mole HCl is added to 1 liter of the resulting solution in problem (17), what will be the OH^- ion concentration?

19. If .01 mole NaOH is added to 1 liter of the resulting solution in problem (17), what will be the final OH^- ion concentration?

20. A hypothetical acid, HA, dissociates as follows:

$$HA = H^+ + A^-$$

(a) If in a 0.1 *M* solution the degree of ionization is 1 percent, calculate the ionization constant for the acid.

(b) Calculate the concentration of the H^+ ion in a .01 *M* solution.

(c) Calculate the degree of ionization in (b).

(d) Calculate the concentration of H^+ ion in a solution which contains 0.1 *M* of the salt NaA and 0.1 *M* of the weak acid HA, the total volume of the mixture being 1 liter.

21. Calculate the molar concentration of a solution of NH_4OH which is known to be 4 percent ionized.

22. What is the molar concentration of a solution of HCN which by experiment is found to be ionized to the extent of .01 percent?

23. Five ml. of 3 *M* HAc is added to 50 ml. of 1 *M* NaAc solution. Calculate the concentration of the H^+ ion in this solution. (The total volume is 55 ml.)

24. Five grams of NH_4Cl is added to 100 ml. of 0.1 *M* NH_4OH solution. Calculate the concentration of the OH^- ion.

25. Fifty ml. of 0.1 *M* HCl is mixed with 75 ml. of 0.1 *M* NH_4OH solution. Calculate the concentration of OH^- ion in the mixture.

26. Repeat problem (25) using NaOH in place of NH_4OH.

27. To 100 ml. of a .02 *M* solution of C_6H_5COOH is added 250 ml. of .02 *M* solution of sodium benzoate (C_6H_5COONa). What is the concentration of the H^+ ion in the resulting solution?

28. 4.75 g. of NH_4Cl is added to a solution already containing 2.5 g. of NH_3 and the total volume is made 500 ml. by the addition of water. What is the concentration of the OH^- ion in this solution?

29. Calculate the *p*H of the following solutions:

(a) 0.1 *M* HCl

(b) A solution containing 1 g. HCl per liter

(c) 0.1 *M* HAc

(d) A solution containing 0.1 *M* HAc and 0.1 *M* NaAc per liter

30. Using HAc and NaAc in different amounts in each case, give the concentrations of each of these substances for three dif-

ferent solutions, each solution having a H^+ ion concentration of 10^{-4}.

31. One hundred ml. of a 0.1 *M* HCl solution is added to 100 ml. of a 0.2 *M* NH_4OH solution.

(a) What fraction of the NH_4OH does the HCl neutralize?

(b) What is the concentration of the NH_4^+ ion? (Neglect that amount of NH_4^+ ion contributed by the NH_4OH not neutralized.)

(c) What is the concentration of the NH_4OH not neutralized?

(d) Calculate the OH^- ion concentration in the resulting solution.

32. In the following problem solid NaOH is to be added gradually to a solution of HAc. As the NaOH is added part of the HAc is neutralized. Even after the final addition of NaOH, the HAc will not be completely neutralized. The H^+ ion concentration and the *p*H of the solution are to be calculated after each addition of NaOH.

One-hundredth of a mole of solid NaOH is added to 1 liter of a 0.1 *M* HAc solution. (Neglect any volume change.)

(a) What fraction of the HAc is neutralized?

(b) What is the concentration of the Ac^- ion? (Neglect that contributed by the HAc not neutralized.)

(c) What is the concentration of the HAc?

(d) Calculate the H^+ ion concentration.

(e) What is the *p*H of the solution?

To the resulting solution another .01 mole of NaOH is added. Again answer (a), (b), (c), (d), and (e). NaOH is added portionwise (.01 mole at a time) until, in all, .07 mole has been added. After the addition of each .01 mole portion calculate the H^+ ion concentration and the *p*H of the solution.

Make a plot of *p*H as the ordinates (vertical axis) against the number of moles NaOH added as abscissae (horizontal axis). Note particularly that the *p*H does not vary greatly between .04 and .06 mole additions of NaOH. This phenomenon will be discussed in a later chapter under "Buffer Solutions."

33. From the data given in Table 20 calculate the approximate values of the indicator constants (K_{Ind}) for the following indicators, assuming them to be weak acids:

(a) methyl orange

(b) brom cresol purple

(c) brom thymol blue

(d) phenolphthalein

(e) thymolphthalein

CHAPTER

8

Heterogeneous Equilibrium — The Solubility Product — Colloids

Any equilibrium which involves some kind of boundary surface is a heterogeneous one. The evaporation of water in a closed vessel is a simple example of this type of equilibrium. Here the water vapor in the enclosing container is in contact with the liquid water through the water surface. Although all heterogeneous equilibria involve boundary surfaces, yet the concentrations of the various substances involved are independent of the area of this surface. For example, the concentration of the water vapor, or the pressure exerted by the water vapor, in any container in which liquid water is also present is independent of the amount of surface exposed by the liquid. The rate at which water evaporates from the surface is greater, the greater the extent of the surface, but the condensation of the water vapor, i.e., the return of the water molecules from the gaseous state to the liquid state, is also greater, the greater the amount of exposed liquid surface. As a result of increasing the surface both the rate of evaporation and the rate of condensation are increased in such a way that the concentration of water remaining in the vapor state is constant.

For a given temperature the rate of evaporation depends only upon the amount of surface exposed; in other words, the rate of evaporation is proportional to the amount of surface

exposed. This statement may be expressed in symbols in the following manner:

$$\text{Rate of evaporation} = k_1 S \tag{1}$$

where k_1 is some proportionality constant and S the amount of surface.

The rate of condensation is proportional to the rate at which vapor molecules strike a unit area of surface and to the amount of surface. The rate at which molecules strike unit area of surface will depend upon the pressure exerted by the vapor. (If, for any given case, the pressure exerted by the vapor is doubled, twice as many molecules strike a unit surface per second.)

$$\text{Rate on unit surface} \propto \text{pressure}$$

Therefore

$$\text{Rate of condensation} \propto P \times S$$

where P is the pressure.

Or
$$\text{Rate of condensation} = k_2 P \times S \tag{2}$$

where k_2 is some proportionality constant. At equilibrium the rate of evaporation equals the rate of condensation and

$$k_1 S = k_2 S \times P$$

Cancelling the surface term S from both sides of the equation,

$$P = \frac{k_1}{k_2} = K_{eq} \tag{3}$$

This means that for a given temperature the vapor pressure of water vapor (or of any liquid) is a constant and is independent of the surface exposed, since the surface factor S does not appear in the final equilibrium equation.

Another type of heterogeneous equilibrium with which we are to deal to a very great extent is the equilibrium between a solid and its ions in solution, i.e., the solubility of some electrolyte in water. To illustrate this type of equilibrium let us consider a specific example, the equilibrium existing

between solid barium sulfate and its saturated solution, and let us apply the Law of Mass Action to this case.

According to the theory of complete ionization, the small amount of barium sulfate which exists in water is present only as barium ions and sulfate ions. Although barium sulfate is very slightly soluble in water, it is nevertheless a salt and therefore is completely ionized. It would be considered as practically completely ionized even on the basis of the theory of incomplete ionization, since its concentration is so small in the saturated solution. When equilibrium conditions are attained, that is, when the solution is saturated with the barium sulfate, the rate at which barium sulfate passes into solution from the solid crystals is equal to the rate at which barium ions and sulfate ions collide and deposit on the surface of the crystal. The rate at which barium ions and sulfate ions leave the solid barium sulfate will depend upon the amount of surface of barium sulfate in contact with the water. If in one case the surface of barium sulfate exposed to the water is three times as great as that in another case, the rate at which it enters the solution will be three times as large.

$$\text{Rate of solution} = k_1 S \tag{4}$$

where S is the amount of surface of barium sulfate exposed to the solution.

The rate of deposition of the barium sulfate will depend upon the rate of which barium ions and sulfate ions collide in juxtaposition on the surface. For a barium ion to deposit, it is also necessary that a sulfate ion deposit next to it, for in the barium sulfate crystals these ions lie next to each other. It would be impossible for only barium ions to deposit, since a positive charge would then develop on the crystal and crystals of barium sulfate could not be formed. The rate of combination of the barium and sulfate ions will then be proportional to the rate at which they collide with each other on the surface of the solid barium sulfate. The rate of formation of the crystal will then be proportional to the concentration of the barium ions, the concentration of the sulfate ions, and the

surface. If the surface is doubled, twice as many collisions between barium ions and sulfate ions occur on the surface in a given period of time. We may then write

$$\text{Rate of deposition} = k_2(Ba^{++})(SO_4^{--})S \tag{5}$$

Under equilibrium conditions the rate of solution equals the rate of deposition, and

$$k_1S = k_2(Ba^{++})(SO_4^{--})S$$

The same amount of surface is involved in both processes of solution and deposition; the S cancels from both sides of the expression and we have

$$(Ba^{++})(SO_4^{--}) = \frac{k_1}{k_2} = K_{S.P.} \tag{6}$$

K_{SP} is an equilibrium constant which is designated more specifically as the solubility product constant, while the product $(Ba^{++})(SO_4^{--})$ under equilibrium conditions is known as the *solubility product.*

Analyzing this expression we see that as the concentration of the barium ion is increased, if equilibrium is to be maintained, the concentration of the sulfate ion must decrease in the inverse ratio. For example, in a saturated solution of barium sulfate in pure water the concentrations of both the barium ions and the sulfate ions are each about 4×10^{-5} mole per liter. The value of $K_{SP.}$ for barium sulfate is then $4 \times 10^{-5} \times 4 \times 10^{-5} = 1.6 \times 10^{-9}$. If now the concentration of the sulfate ions in this same solution is increased tenfold, that is, to 4×10^{-4} mole per liter by the addition of a small amount of sodium sulfate, then to maintain equilibrium the concentration of the barium ions must be decreased tenfold to 4×10^{-6} mole per liter, and now $(Ba^{++})(SO_4^{--}) = 4 \times 10^{-6} \times 4 \times 10^{-4} = 1.6 \times 10^{-9}$.

The product of the two concentrations must always equal 1.6×10^{-9}, the solubility product constant for the temperature in question. A decrease in the concentration of barium ions by the addition of sulfate ions, as just described, can only take

place by the precipitation of barium sulfate. In other words, the barium ions can be removed from the solution only by the formation of solid barium sulfate. This general conclusion can be qualitatively deduced from a consideration of the Rule of Le Chatelier. The equilibrium is represented by the equation,

$$BaSO_4(\text{solid}) = Ba^{++} + SO_4^{--} \tag{7}$$

By increasing the concentration of the sulfate ions the equilibrium is shifted to the left, i.e., solid barium sulfate is formed, and this shift proceeds until a new equilibrium condition is established which, in the case cited above, results in a concentration of 4×10^{-4} mole per liter for sulfate ions and 4×10^{-6} mole per liter for barium ions.

We may apply the Law of Mass Action directly to this equilibrium without considering the rate processes involved and arrive at the same conclusion. Applying the Law of Mass Action to the equilibrium for equation (7) we may write

$$\frac{(Ba^{++})(SO_4^{--})}{(BaSO_4, \text{solid})} = k_1 \tag{8}$$

or

$$(Ba^{++})(SO_4^{--}) = k_1(BaSO_4, \text{solid})$$

But the concentration of solid barium sulfate does not change. Its concentration depends only upon the density of solid barium sulfate, which remains practically constant under all ordinary conditions. Therefore the product $k_1 \times (BaSO_4, \text{solid})$ is a constant, which we designate as $K_{S.P.}$ or

$$(Ba^{++})(SO_4^{--}) = K_{S.P.} \tag{9}$$

This is the same expression as that previously obtained (equation 6).

Applying these same considerations to silver chromate which dissolves slightly in water to give two silver ions for each chromate ion,

$$Ag_2CrO_4(\text{solid}) = 2Ag^+ + CrO_4^{--} \tag{10}$$

we obtain

$$(Ag^+)^2(CrO_4^{--}) = K_{S.P.} \tag{11}$$

In this case, however, for the deposition of silver chromate from its solution it is necessary that two silver ions and one

chromate ion collide on the surface of the solid silver chromate, and therefore the concentration of the silver ion is squared.

Conditions Necessary for Precipitation. Every pure substance has a definite solubility in water at a given temperature. When the concentration of the substance in water solution exceeds this solubility value, either precipitation of the substance from solution or a supersaturated solution will be the result. The solubility product is a quantitative statement of the limit of solubility of any difficultly soluble substance which forms ions. When the product of the concentrations of the ions in the solution exceeds the value of the solubility product constant either precipitation will ensue or a supersaturated solution will be formed. Supersaturated solutions form with difficulty and precipitation is the usual result of excess concentration of the ions.

To illustrate this condition let us consider a specific example. If a solution contains chloride ion at a concentration of 10^{-5} mole per liter in the form of dissolved sodium chloride or calcium chloride, will a precipitate be formed when enough silver nitrate is added to make the silver ion concentration equal to 10^{-3} mole per liter? The condition necessary for precipitation is

$$(Ag^+)(Cl^-) = K_{S.P.} \qquad (12)$$

The solubility product constant for silver chloride at room temperature is 2.8×10^{-10}. In the solution under consideration $(Ag^+)(Cl^-) = 10^{-3} \times 10^{-5} = 10^{-8}$, which is greater than 2.8×10^{-10}. We see that the product of the silver ion concentration and the chloride ion concentration exceeds the solubility product constant; hence, either precipitation will follow or a supersaturated solution will be formed.

If, in the above case, the concentration of the silver ion were made 10^{-5} mole per liter rather than 10^{-3} mole per liter, no precipitation would take place under any circumstances, for now the product $(Ag^+)(Cl^-)$ would be less than the solubility product constant,

$$(Ag^+)(Cl^-) = 10^{-5} \times 10^{-5} = 10^{-10} < 2.8 \times 10^{-10}$$

Supersaturation of Difficultly Soluble Substances. As we have already indicated, precipitation will not always occur when the concentrations of the ions exceed the solubility product constant, due to the slow rate of precipitation. However, once the small crystals are formed, the precipitation

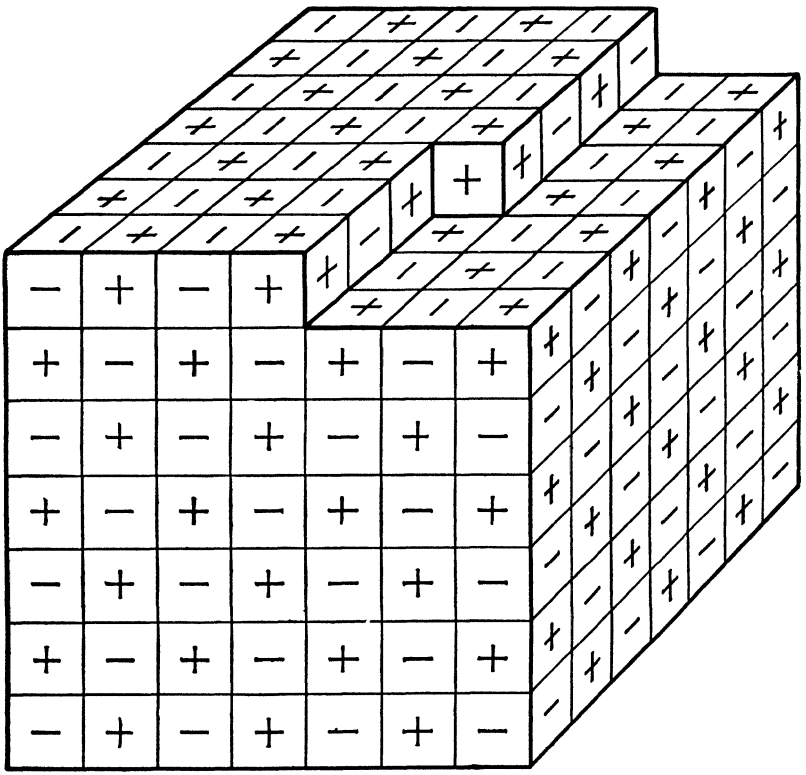


FIG. 8.1 Schematic representation of a crystal.

proceeds rapidly. The process of forming the first nucleus about which crystallization takes place is entirely different from the later crystallization. Any crystal which is within the limit of visibility even with the best microscope contains thousands of ions. Such a crystal is pictured in a general way in Figure 8.1.

In this case the ions only need find their regular positions

and thus build up the crystal. When the crystal is started, however, the situation becomes entirely different. Figure 8.2 illustrates in a general way an incipient crystal. Here the forces holding the ions are certainly different since each ion occupies a corner and edge position. An additional condition is that four or more ions be sufficiently close to each other simultaneously to allow the nucleus to form. This situation is probably rather rare. We see from these illustrations that the process of incipient crystallization is undoubtedly a more complicated phenomenon than is usually imagined. Barium oxalate, BaC_2O_4, and calcium chromate, $CaCrO_4$, are two well-known examples of difficultly soluble salts which easily form supersaturated solutions.

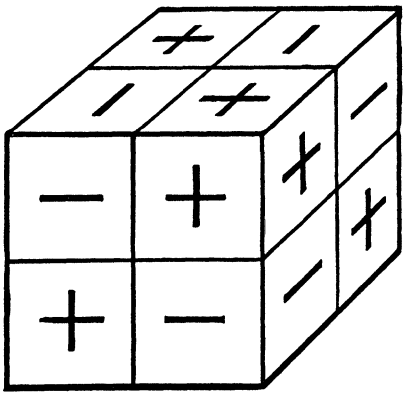


FIG. 8.2 Formation of first crystal nucleus.

Solubility of Very Small Crystals. Experiments have shown definitely that small crystals of any substance are more soluble than larger ones. Barium sulfate crystals, 10^{-4} cm. in diameter, are almost twice as soluble as crystals twenty times this diameter. The difference between the solubility of crystals 10^{-3} cm. in diameter and the solubility of larger crystals becomes inappreciable and it is only for very small crystals that this factor must be considered. Calculations have shown that ions in the interior of a crystal are bound with greater forces than are those on the faces or edges. Evidently a greater fraction of the ions occupy external positions for small than for larger crystals, and therefore the average tendency to enter the solution will be greater for the smaller crystal. From these considerations it can be deduced that crystals will grow in such a way as to produce as many interior ions (as few surface ions) as possible. Such a condition is attained only by the growth of larger crystals at the expense of smaller ones.

Since small crystals are more soluble than large crystals, the smallest crystals will in time dissolve and the larger ones will grow still larger. No real equilibrium is attained until the crystals are relatively large. Minute crystals will pass through filters and it is often possible to "digest" such precipitates to remove this condition. Heat increases the rate of solution, crystallization, and the rate at which the large crystals will grow from the smaller ones. Very often the precipitate will become sufficiently coarse, i.e., digested, either by heating or allowing the suspended precipitate to stand overnight.

The fact that small crystals have a greater solubility means that a different and larger solubility product constant must apply to these than to the larger crystals. The solubility product constants are calculated for solutions in contact with relatively large crystals. When calculating the concentrations of the different ions necessary for precipitation it must be borne in mind that a slight excess concentration over that demanded by the solubility product constant is required, since the first crystals formed are necessarily small. However, after crystallization has set in and relatively larger crystals are formed, the concentrations of the ions left in solution will be in accord with the solubility product constant.

Limit of Visibility of Precipitates Is Often the Determining Factor in Qualitative Analysis. Even though a precipitate may form from very dilute solutions of the reactants, yet that precipitate may exist in such small quantities that it is not visible. Such a precipitate would be of no consequence in qualitative analysis. For example, calculations show that a precipitate will be formed when a solution which contains as little as 10^{-20} mole per liter of copper ion, Cu^{++}, is saturated with hydrogen sulfide. Obviously, such a precipitate could not be seen. With silver chloride a precipitate is only visible when the solution before precipitation contains either silver ion or chloride ion at a concentration greater than 2×10^{-5} mole per liter. For the detection of a precipitate it is necessary that the ions producing the precipitate be present at concentrations sufficient to render the solid phase visible.

The lower limit of "visible" concentration is about 10^{-4} mole per liter for most substances.

Increase in Solubility by the Formation of Weak Acids. The addition of any acid to a saturated solution will increase the solubility of the salt if the hydrogen ion combines with the anion of the salt to form a weak acid. Thus, the equilibrium between silver acetate and its ions,

$$AgAc(solid) = Ag^+ + Ac^- \qquad (13)$$

is shifted to the right by the addition of hydrogen ion in the form of a strong acid, such as nitric acid since the hydrogen ions combine with the acetate ions to form acetic acid.

All carbonates are soluble in acid solution due to the formation of the weak acid, carbonic acid, $H_2CO_3(CO_2 + H_2O)$. Barium carbonate is readily dissolved by hydrochloric and by nitric acid solutions. The solubility of barium sulfate, on the other hand, is not increased appreciably by the addition of hydrochloric acid because sulfate ions show little tendency to combine with hydrogen ions.

The solubility of any sulfide is increased by the addition of hydrogen ion, since the weak acid, hydrogen sulfide, and its weak ion, HS^-, are formed. In some cases, however, the sulfide may be so insoluble that an increase in its solubility as much as a millionfold will not be appreciable. In other words, for the very insoluble sulfides the addition of acid to the solution does not allow an appreciable amount of the sulfide to dissolve even though the solubility is increased enormously. Equilibria involving the sulfides will be considered in detail in a later chapter.

Colloids. If any relatively insoluble substance is prepared in a finely divided state and added to a liquid, such as water, a suspension of the solid in the liquid will be formed, which will ultimately settle to the bottom of the container provided that the suspended material is not too finely divided. Very finely divided suspended material will remain in continued suspension if no subsequent coagulation of the particles takes place. Such a system is a heterogeneous one and the substance in the finely

divided state is known as the ***dispersed phase*** and the liquid, the ***dispersing medium.***

When the particles in the dispersed phase are so small that they can no longer be seen or detected with the microscope, we may well ask whether this system is a suspension or a solution. If the particles were of molecular size, the system would be a solution, and if the particles were visible, a suspension or mixture would be formed. There is no sharp distinction between solutions and suspensions, and systems for which the suspended particles lie in this intermediate condition are known as ***colloidal suspensions*** or ***colloidal solutions.*** The finely divided dispersed phase in such a system is known as a ***colloid.***

As we have said previously, molecules or ions at the surface of a crystal or particle behave somewhat differently from those in the interior. The properties of any substance which has a large surface compared to its volume are more like those of the surface molecules. A very finely divided substance has a very much larger surface than one consisting of large particles. Since colloidal particles are very finely divided the increased surface is responsible for some of the properties which distinguish this class of substances from substances as we ordinarily know them. For simplicity, let us consider the total surface area of the cubic particles contained in one $cm.^3$ of a given substance. If only one particle is present, each edge has a length of 1 cm. and the surface area of the cube is 6 $cm.^2$ By decreasing the size of the particle, the number of particles in one $cm.^3$ and the surface area are greatly increased, as is demonstrated by Table 21 on page 167.

While the limit of distinct visibility with the microscope is about 10^{-5} cm., yet particles somewhat smaller than this can be detected but not seen in outline. Such very small particles when viewed through a microscope with illumination from the side will reflect light and sparkle. Such a microscopic arrangement is known as the ultra-microscope.

The Brownian Movement. When very small particles are viewed through the microscope or ultra-microscope, they appear to be darting about in constant zig-zag motion. This

TABLE 21

SURFACE OF ONE CM.^{3} OF MATERIAL FOR DIFFERENT PARTICLE SIZES

Size of Cubic Particle, cm.	Surface, cm.^{2}
1	6
0.1	60
0.01	600
0.001	6000
0.0001	60000
0.00001 *	600000
0.000001	6000000

* Limit of visibility.

motion of small particles is known as the Brownian Movement and is characteristic of all colloidal suspensions. When we seek an explanation of this motion we are led back to the kinetic theory of matter, which postulates that all molecules are in motion. Any particle in suspension is bombarded on all sides by the moving molecules of the dispersing medium. When the particles are sufficiently large the impact of the molecules on the side of the particle is not great enough to cause any appreciable movement. Furthermore, the bombardment on one side of the particle is counterbalanced by the bombardment on the opposite side, so the net result is that there is no appreciable momentum imparted to the particle in any particular direction. When the particle is very small the probability that it will be struck simultaneously with equal force on two opposite sides becomes small, and since the particle itself is small its velocity acquired by impact will be large and a visible motion results.

Classes of Colloids. Colloidal systems are not confined to the suspension of solids in liquids, although such suspensions are of most importance in qualitative analysis and in most problems in chemistry. One liquid dispersed in another is

known as an emulsion; mayonnaise dressing is an example of an emulsion, essentially an oil in water. The different general types of colloidal systems are given below in tabular form.

TABLE 22

TYPES OF COLLOIDAL SYSTEMS

Dispersing Phase	Dispersed Phase	Type
gas	gas	none (homogeneous)
gas	liquid	fog
gas	solid	smoke
liquid	gas	foam
liquid	liquid	emulsion (mayonnaise dressing)
liquid	solid	suspension (muddy water)
solid	gas	solidified foam (pumice)
solid	liquid	
solid	solid	ruby glass

Adsorption. Any molecule, atom, or ion may be conceived as being surrounded by a field of force, which field is not neutralized or "satisfied" when the particle is existing alone in space. This attractive force varies considerably with different particles. Thus the helium atom has a very small field, as evidenced by its very low boiling point, while the molecules of a substance having a high melting point or high boiling point possess relatively large attractive forces. When a molecule or ion is situated in the interior of a crystal these forces are neutralized or satisfied to the greatest possible extent. At the surface of a crystal, however, the attractive forces are not completely neutralized and the residual force of the surface molecules attracts other particles and holds them fast to the surface. This adherence of foreign particles to any surface is known as ***adsorption.*** The smaller the particle the greater will be the amount of surface and the larger the total effect of surface forces. Not all finely divided particles are perfect crystals and the less perfect the crystalline form the greater

will be the adsorptive forces, for under such conditions the the attractive forces of the molecules in the crystal are less satisfied by each other. Gelatinous precipitates like aluminum hydroxide and ferric hydroxide are very probably imperfectly crystallized and these substances have very great adsorptive capacities.

The small size of colloidal particles, because of the increased surface area, makes them particularly good adsorbents. Not only are neutral molecules adsorbed to their surfaces but ions as well. The adsorption of ions on the surface of colloidal particles is preferential, i.e., not all ions are adsorbed alike. In some cases negative ions are adsorbed more readily than positive ions. In such cases the colloidal particles become negatively charged. Some colloids, on the other hand, become positively charged through the adsorption of positive ions. If all the colloidal particles have the same charge, they will repel each other and prevent coagulation. The adsorption of ions of like charge, therefore, stabilizes the colloidal solution. When placed in an electric field — between two charged plates — negatively charged particles will move toward the positive plate and positively charged particles toward the negative plate. Under some conditions these particles become neutralized at the electrode and "plate out" just as ions may be plated from solution. By such a process rubber may be "plated out" of its suspension.

Finely divided barium sulfate has a great tendency to adsorb other ions from solution. In fact this tendency is so great that it becomes very difficult to obtain pure barium sulfate by precipitation.

Coagulation of Colloids. Not all colloidal suspensions are stable. Many of them tend to coagulate through the adherence of the particles for each other. When silver chloride is precipitated from solution it first forms a very finely divided suspension but in a short time these fine particles coagulate and settle to the bottom of the container. This process is hastened by heating, and in many instances this simple expedient is sufficient to cause coagulation.

When a negatively charged colloid such as arsenic trisulfide, As_2S_3, is in suspension, it may be coagulated by adding certain positive ions to the solution in the form of salts, acids or bases, which have a tendency to be adsorbed. The adsorbed positive ions neutralize the negative ions already adsorbed and the more nearly neutral particles then coagulate. In general, the hydrogen ion is highly adsorbed and the addition of an acid to this suspension precipitates it.

In general, those ions which are multiply charged are more effective in causing coagulation than singly charged ions. Aluminum ion is more effective than magnesium ion, Mg^{++}, and this ion in turn is more effective than sodium ion, Na^{+}.

In qualitative analysis finely divided precipitates are often very troublesome and annoying. Coagulation may often be effected by either heating or by the addition of an acid. It is evident that salts can very seldom be added to the solution, since in most cases they will interfere with the analysis.

The applications of dyestuffs to cloth fiber is usually a process of adsorption, the dyestuff being adsorbed on the fiber. Dyes will not "take" to certain fibers and in such a case the material to be dyed may be coated with a coagulant such as aluminum hydroxide or stannic acid, which in turn will adsorb the dye and bind it to the cloth fiber. Coagulants used for such purposes are known as ***mordants*** and the combination between the mordant and the dye is called a ***lake.***

In qualitative analysis use is made of the adsorptive properties of aluminum hydroxide in its detection. This substance possesses the property of adsorbing a dyestuff known as aluminon. When the latter is added to a suspension of aluminum hydroxide, $Al(OH)_3$, it is adsorbed preferentially by the hydroxide and the suspension, which is a lake, assumes a characteristic red color.

Catalysts. Preferential adsorption is the property that gives contact catalysts their special effectiveness. The substances which react with each other are adsorbed on the surface of the catalyst and the products formed are adsorbed to a lesser extent and thus leave the surface of activity.

The preparation of a catalyst usually greatly influences its activity. If the catalyst is prepared in such a way that the substance formed is not well crystallized, it usually becomes more active. Thus, when iron is used as a catalyst it is most active when prepared from iron oxalate. This compound is broken down at low temperatures to ferric oxide, carbon monoxide and carbon dioxide, and the ferric oxide in turn is reduced with hydrogen at a low temperature. At the low temperature perfect iron crystals form with difficulty; the imperfect crystals are the better adsorbers, hence the greater their catalytic activity. The addition of foreign substances such as sodium hydroxide or aluminum oxide often enhances this activity of the catalyst. These substances, known as ***promoters,*** very probably prevent the formation of perfect or large crystals by keeping the iron atoms apart.

Examples of Problems Involving the Solubility Product Principle

Example 1.

The solubility of $BaSO_4$ in water is .00092 g. per 100 ml. What is the value of the $K_{S.P}$ for $BaSO_4$?

First, calculate the solubility of $BaSO_4$ in moles per liter. .00092 g. per 100 ml. is equivalent to .0092 g. per liter.

The molecular weight of $BaSO_4$ is 233.4.

$$\frac{9.2 \times 10^{-3}}{233.4} \text{ mole per liter} = 3.9 \times 10^{-5} \text{ mole per liter}$$

This means that there is 3.9×10^{-5} mole each of the barium ion and sulfate ion in solution.

The solubility product constant is therefore

$$(Ba^{++})(SO_4^{--}) = 3.9 \times 10^{-5} \times 3.9 \times 10^{-5} = 1.5 \times 10^{-9}$$

Example 2.

Silver chromate, Ag_2CrO_4, is soluble to the extent of .0259 g. per liter. Calculate the solubility product constant.

The molecular weight of silver chromate is 331.8. The solubility in moles per liter is

$$\frac{.0259 \text{ g. per liter}}{331.8 \text{ g. per mole}} = 7.8 \times 10^{-5} \text{ mole per liter}$$

Since silver chromate is completely ionized there is 7.8×10^{-5} mole of chromate ion and $2 \times 7.8 \times 10^{-5}$ mole of silver ion in solution.

The $K_{S.P.}$ is then

$$(Ag^+)^2(CrO_4^{--}) = (2 \times 7.8 \times 10^{-5})^2 \times 7.8 \times 10^{-5} = 1.9 \times 10^{-12}$$

Example 3.

Calculate the solubility of $SrSO_4$ in g. per 100 ml. from its solubility product constant. $K_{S.P.} = 7.6 \times 10^{-7}$.

Let X be the number of moles of $SrSO_4$ in 1 liter of solution.

Since $SrSO_4$ is completely dissociated, there will be X moles of Sr^{++} ion and X moles of SO_4^{--} ion in solution.

$$\begin{gathered} SrSO_4(\text{solid}) = Sr^{++} + SO_4^{--} \\ X \quad \rightarrow \quad X \quad X \\ (Sr^{++})(SO_4^{--}) = X^2 \\ X^2 = 7.6 \times 10^{-7} = 76 \times 10^{-8} \\ X = 8.7 \times 10^{-4} \text{ mole per liter} \end{gathered}$$

This is not only the concentration of the strontium ion and of the sulfate ion, but it also represents the concentration of the total amount of strontium sulfate in solution. The molecular weight of strontium sulfate is 184. There are therefore

$8.7 \times 10^{-4} \times 184 = 0.16$ g. $SrSO_4$ per liter or .016 g. per 100 ml.

Example 4.

Calculate the solubility of $Mg(OH)_2$ in g. per liter from the solubility product constant. ($K_{S\ P.} = 8.9 \times 10^{-12}$).

X = number of moles of $Mg(OH)_2$ dissolved — (total)
X = number of moles of Mg^{++} ion in solution at equilibrium
$2X$ = number of moles of OH^- ion in solution at equilibrium

$$\begin{gathered} (Mg^{++})(OH^-)^2 = X(2X)^2 = 4X^3 = 8.9 \times 10^{-12} \\ X^3 = 2.2 \times 10^{-12} \\ X = 1.3 \times 10^{-4} \text{ mole per liter} \end{gathered}$$

The molecular weight of $Mg(OH)_2$ is 58.3. Therefore the solubility is

$$1.3 \times 10^{-4} \times 58.3 = 76 \times 10^{-4} = .0076 \text{ g. per liter}$$

Example 5.

What is the concentration of the Ag^+ ion in moles per liter left in solution if AgCl is precipitated by adding enough HCl to a solution of $AgNO_3$ to make the final Cl^- ion concentration 0.1 molar?

$$K_{S\,P}\,(AgCl) = 2.8 \times 10^{-10}$$
$$(Ag^+)(Cl^-) = 2.8 \times 10^{-10}$$
$$(Ag^+) \times 0.1 = 2.8 \times 10^{-10}$$
$$(Ag^+) = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \text{ mole per liter}$$

Example 6.

(a) A solution contains .01 mole Cl^- ion and .001 mole CrO_4^{--} ion per liter. Ag^+ ion is gradually added to this solution in the form of $AgNO_3$. Which will be precipitated first, AgCl or Ag_2CrO_4?

$$K_{S\,P.}\,(AgCl) = 2.8 \times 10^{-10}$$
$$K_{S\,P}\,(Ag_2CrO_4) = 1.9 \times 10^{-12}$$

(1) Calculate (Ag^+) necessary to precipitate AgCl.

$$(Ag^+)(Cl^-) = (Ag^+) \times .01 = 2.8 \times 10^{-10}$$

$$(Ag^+) = \frac{2.8 \times 10^{-10}}{.01} = 2.8 \times 10^{-8} \text{ mole per liter}$$

(2) Calculate (Ag^+) necessary to precipitate Ag_2CrO_4.

$$(Ag^+)^2(CrO_4^{--}) = (Ag^+)^2 \times .001 = 1.9 \times 10^{-12}$$
$$(Ag^+)^2 = \frac{1.9 \times 10^{-12}}{10^{-3}} = 1.9 \times 10^{-9} = 19 \times 10^{-10}$$

$$(Ag^+) = 4.35 \times 10^{-5} \text{ mole per liter}$$

A greater concentration of Ag^+ ion is necessary to cause precipitation of Ag_2CrO_4 than AgCl, so AgCl will precipitate first.

(b) What will be the concentration of the Cl^- ion in this solution when the Ag_2CrO_4 begins to precipitate by the continued addition of $AgNO_3$? Bear in mind that as the AgCl is precipitated by the addition of Ag^+ ion the Cl^- ion concentration is reduced.

The Ag^+ ion concentration necessary to precipitate the Ag_2CrO_4 is 4.35×10^{-5} mole per liter. For this concentration of Ag^+ ion the Cl^- ion concentration will be

$$(Cl^-) = \frac{2.8 \times 10^{-10}}{(Ag^+)} = \frac{2.8 \times 10^{-10}}{4.35 \times 10^{-5}} = 0.644 \times 10^{-5}$$

$$= 6.44 \times 10^{-6} \text{ mole per liter}$$

(c) What fraction of the amount of Cl^- ion originally present remains in solution when Ag_2CrO_4 begins to precipitate?

(Cl^-) (original) = .01 mole per liter

(Cl^-) when precipitation of Ag_2CrO_4 begins = 6.44×10^{-6} mole per liter

$$\frac{6.44 \times 10^{-6}}{.01} = 6.44 \times 10^{-4} = .000644$$

= .0644 percent of original Cl^- ion present.

Calculations Involving Both the Ionization Constant and Solubility Product Constant

Example 7.

How many moles of NH_4Cl must be added to 100 ml. of 0.1 *M* NH_4OH solution to prevent precipitation of $Mn(OH)_2$ when this solution is added to 100 ml. of a .02 *M* solution of $MnCl_2$?

$$K_{SP.}\ (Mn(OH)_2) = 2 \times 10^{-13}$$
$$K_I\ (NH_4OH) = 1.8 \times 10^{-5}$$

In working this problem consider the concentrations of all substances in the final solution after the two original solutions are mixed. The concentration of the Mn^{++} ion will be .01 *M* and the OH^- ion just necessary to begin the precipitation of the $Mn(OH)_2$ can be calculated from its solubility product constant.

$$(Mn^{++}) \times (OH^-)^2 = .01 \times (OH^-)^2 = 2 \times 10^{-13}$$
$$(OH^-)^2 = 20 \times 10^{-12}$$
$$(OH^-) = 4.5 \times 10^{-6} \text{ mole per liter}$$

If the (OH^-) exceeds this calculated value, $Mn(OH)_2$ will be precipitated. To prevent precipitation, the (OH^-) must be less than this value. The (OH^-) can be diminished by the addition of NH_4^+ ion, in the form of NH_4Cl. The concentration of the NH_4^+ ion is equilibrium with this low concentration of OH^- ion can be calculated from the K_I for NH_4OH.

$$\frac{(NH_4^+)(OH^-)}{(NH_4OH)} = 1.8 \times 10^{-5}$$

The concentration of the NH_4OH is practically .05 mole per liter.

$$\frac{(NH_4^+) \times 4.5 \times 10^{-6}}{.05} = 1.8 \times 10^{-5}$$

$$(NH_4^+) = \frac{1.8 \times 10^{-5} \times .05}{4.5 \times 10^{-6}}$$

$$= 0.2 \text{ mole per liter}$$

$$= .040 \text{ mole per 200 ml.}$$

Since this is the total amount of NH_4^+ ion which must be added in the form of NH_4Cl, it is this amount which must be added to the original 100 ml. of NH_4OH. The amount of NH_4^+ ion formed by the dissociation of NH_4OH is negligibly small and therefore has been neglected in the calculations.

Questions and Problems

(In all of the following problems in this Chapter the hydrolysis of the ions is neglected)

1. What is a heterogeneous equilibrium?
2. If solid barium sulfate is in equilibrium with its ions, Ba^{++} and SO_4^{--}, in solution, will this equilibrium be effected by the addition of more solid barium sulfate?
3. If in a saturated solution of silver chloride, the concentrations of the Ag^+ ion and Cl^- ion are each 1.67×10^{-5} M, what will be the final concentration of the Ag^+ ion if sufficient sodium chloride is added to the solution to increase the Cl^- ion concentration one hundredfold?
4. What are the conditions necessary for the precipitation of a relatively insoluble salt?
5. If the product of the concentrations of the ions exceeds the solubility product will precipitation always occur? Explain.
6. Is the solubility product for very small crystals the same as that for large crystals?
7. Explain why small crystals would be expected to be more soluble than large crystals.
8. What is the order of magnitude of the concentration of the ions necessary to produce a precipitate visible to the naked eye?
9. If a cube 1 cm. on the side is divided into one million cubes each of the same size, how much is the total surface increased?

10. Why do the surfaces of imperfect crystals adsorb substances to a greater extent than do those of perfect crystals?

11. How may colloids be coagulated?

12. Explain the use of "aluminon" reagent in qualitative analysis.

13. Why are catalysts more active when prepared at low temperatures?

14. The solubility of each of the following salts is given below in terms of grams per 100 ml. of solution. Calculate the solubility product constant for each substance.

Substance	*Solubility in grams per 100 ml.*
(a) AgCl	2.40×10^{-4}
(b) AgBr	1.35×10^{-5}
(c) AgI	2.15×10^{-7}
(d) $BaSO_4$	8.95×10^{-4}
(e) Ag_2CrO_4	2.56×10^{-3}
(f) $CaCO_3$	8.3×10^{-4}
(g) SrF_2	7.3×10^{-3}

15. The solubility product constants are given below for a few difficultly soluble substances. Calculate the solubility of each in terms of grams of solute per 100 ml. of solution.

Substance	*Solubility Product Constant*
(a) $Mg(OH)_2$	8.9×10^{-12}
(b) $BaCO_3$	1.6×10^{-9}
(c) Ag_2CrO_4	1.9×10^{-12}
(d) $Fe(OH)_3$	6×10^{-38}
(e) MgC_2O_4	8.6×10^{-5}
(f) $SrSO_4$	7.6×10^{-7}
(g) CuI	1×10^{-12}
(h) AgCN	1.6×10^{-14}

16. The solubility product constant for $BaCrO_4$ is 8.5×10^{-11}. If the concentration of the barium ion in a solution is .04 *M*, calculate the minimum concentration of the chromate ion, in terms of moles per liter, that will be required to begin the precipitation of barium chromate, assuming that a supersaturated solution is not formed. How many grams of sodium chromate must be added to 200 ml. of water to produce this amount of chromate ion?

17. How many grams of silver chromate will dissolve in 100 ml. of 0.1 *M* potassium chromate solution?

18. (a) Calculate the number of grams of PbS that would precipitate from 1 liter of saturated solution of PbI_2, if the solution is saturated with H_2S, assuming that the concentration of the sulfide ion is kept at 1×10^{-15} mole per liter.
(b) How many moles of Pb^{++} are left in solution?

19. Calculate the number of moles of AgCl that will dissolve (a) in 1 liter of 0.1 *M* KCl solution; (b) in 1 liter of 0.1 *M* $CaCl_2$ solution.

20. If $AgNO_3$ is added slowly to each of the following solutions, calculate the concentration of the Ag^+ ion in the resulting solution just after the first trace of precipitate appears.
(a) 0.1 *M* KBr solution. (b) 0.1 *M* K_2CrO_4 solution.
(c) A solution containing 1 mole HCl and .001 mole KI per liter.

21. The solubility of PbI_2 is .058 g. per 100 ml. at room temperature.
(a) What is the concentration of Pb^{++}? Of I^-?
(b) Write the solubility product expression for PbI_2.
(c) Calculate the solubility product constant for PbI_2.

22. The solubility product constant for calcium oxalate at room temperature is 1.3×10^{-9}.
(a) What is the concentration of Ca^{++} and of $C_2O_4^{--}$ in a saturated solution of calcium oxalate?
(b) Calculate the number of grams of calcium oxalate dissolved in a liter of saturated solution.

23. The solubility product constant for lead iodate at room temperature is 2.6×10^{-13}. How many grams of lead iodate are required to make 200 ml. of a saturated solution?

24. Calculate the concentration of the OH^- in a saturated solution of silver hydroxide.

25. How many grams of NaOH are required to start the precipitation of $Mg(OH)_2$ in 100 ml. of a solution which contains 0.1 g. of $MgCl_2$?

26. If to a liter of solution containing 0.1 mole of Ag^+ enough Cl^- is added to make the final concentration of the Cl^- ion remaining in solution 1×10^{-4} mole per liter, what fraction of Ag^+ is left in solution? (Assume no volume change.)

27. $AgNO_3$ is added to a solution containing .001 mole Cl^- and .001 mole Br^- per liter. What are the concentrations of Cl^- and of Br^- remaining when the AgCl just begins to precipitate?

28. How many grams of Ag^+ are present in (a) 5 ml. of a saturated solution of AgBr?
(b) 5 ml. of a saturated solution of AgCl?

29. How many moles of AgCl would dissolve in 1 liter of the following solutions:
(a) 0.1 *M* NaCl
(b) 0.1 *M* KNO_3
(c) Pure water
(d) 0.1 *M* $AgNO_3$
(e) 1×10^{-5} *M* HCl

30. Solid AgCl is added to a 0.1 *M* KBr solution. What is the ratio of the (Cl^-) to the (Br^-) in the solution when equilibrium is attained?

31. The solubility of the AgI is 2.15×10^{-7} g. per 100 ml. in water, and that of AgCl is 2.4×10^{-4} g. per 100 ml. Assuming that there is no volume change when pulverized solid $AgNO_3$ is added little by little to 1 liter of a solution containing 0.1 mole of KCl and 0.1 mole of KI:
(a) At what concentration of Ag^+ will AgI first precipitate?
(b) At what concentration of Ag^+ will AgCl begin to precipitate?
(c) Which precipitates first, AgI or AgCl?
(d) What will be the concentration of I^- when AgCl starts to precipitate?
(e) What percentage of the I^- initially present will remain in solution when AgCl begins to precipitate?
(f) What will be the ratio of the concentration of Cl^- to that of I^- in the solution when AgCl begins to precipitate? (Use result of (d) to obtain answer.)
(g) When half of the Cl^- initially present has been precipitated as AgCl, what will be the concentration of (1) Ag^+ and (2) I^- in the supernatant liquid?
(h) What is the ratio of the concentration of Cl^- to that of I^- in the supernatant liquid of part (g)?

32. The solubility of PbI_2 is 1.28×10^{-3} mole per liter and that of AgI 9.2×10^{-9} mole per liter at room temperature. Assuming that there is no volume change when solid NaI is added slowly to 1 liter of a solution which is .01 *M* in Pb^{++} and .01 *M* in Ag^+:
(a) At what concentration of I^- will AgI first precipitate?
(b) At what concentration of I^- will PbI_2 first precipitate?
(c) Which will precipitate first, AgI or PbI_2?
(d) What will be the concentration of Ag^+ in the solution when PbI_2 first starts to precipitate?

(c) What is, therefore, the ratio of the concentration of Pb^{++} to that of Ag^+ at this point?

(f) When the concentration of Pb^{++} has been reduced to half of its original value, what will be the concentration of I^-?

(g) Then what will the concentration of Ag^+ be at this concentration of Pb^{++}?

(h) What is then the ratio of the concentration of Pb^{++} to that of Ag^+ at the point described in parts (f) and (g)? Compare with the answer to part (e).

(i) When AgI and PbI_2 precipitate together, show from the solubility product constants that the concentration of the Ag^+ is always proportional to the square root of the concentration of the Pb^{++} under these conditions.

(j) Why are the ratios found in parts (c) and (h) not the same, whereas similar ratios in Problem 31 were found equal?

33. How many moles of AgAc will dissolve in a liter of a 0.1 *M* HNO_3 solution? (The $K_{S\,P}$ for AgAc is 4×10^{-3}.) (Note that in the resulting solution the concentration of HAc (unionized) is approximately 0.1 *M*.)

34. A solution contains .01 *M* Mg^{++} and .05 *M* NH_4Cl. How much NH_4OH must be added to 1 liter of this solution to begin the precipitation of $Mg(OH)_2$?

35. How many grams of NH_4Cl must be added to 50 ml. of 0.2 *M* NH_4OH to prevent the precipitation of $Mn(OH)_2$ when this solution is added to 50 ml. of .02 *M* $MnCl_2$ solution?

36. If 50 g. of $MgCl_2$ and 50 ml. of 6 *M* NH_4OH are added to enough water to make 1 liter of solution, how much NH_4Cl in grams must be added to this same solution to prevent precipitation of $Mg(OH)_2$? (Assume no volume change.)

37. A solution is .01 *M* in hydrogen ion and 0.1 *M* with respect to acetic acid. Calculate the concentration of the silver ion, in moles per liter, that will be required to just start precipitation of silver acetate.

CHAPTER

9

Polybasic Acids — Precipitation with Hydrogen Sulfide

Polybasic acids are those acids the molecules of which have more than one replaceable hydrogen atom and therefore dissociate to produce hydrogen ions in more than one step. Dibasic acids and tribasic acids, which are special classes of polybasic acids, have two and three replaceable hydrogen atoms respectively. Phosphoric acid, an example of a tribasic acid, dissociates to produce hydrogen ion in three steps, which are represented by the equations:

$$H_3PO_4 = H_2PO_4^- + H^+ \quad (1)$$

$$H_2PO_4^- = HPO_4^{--} + H^+ \quad (2)$$

$$HPO_4^{--} = PO_4^{---} + H^+ \quad (3)$$

The process represented by equation (1) takes place to a greater extent than either (2) or (3), and (2) to a greater extent than (3). The ions, $H_2PO_4^-$ and HPO_4^{--}, resulting from the dissociation of phosphoric acid, are likewise acids and the relative strengths of H_3PO_4 and these ions as acids can be readily determined by a consideration of the three dissociation constants for phosphoric acid. The dissociation constant for the process represented by equation (1) is 7.5×10^{-3}; for the process represented by equation (2), 6.2×10^{-8}; and for (3), 1×10^{-12}. A 0.1 molar solution of phosphoric acid dissociates according to equation (1) to the extent of about 25 percent, while

the concentration of PO_4^{---} in this same solution produced by step (3) is only about 10^{-18} molar. This small concentration of PO_4^{---} ion is the reason that most insoluble phosphates cannot be precipitated from phosphoric acid solution.

Sulfuric acid, the commonest example of a dibasic acid, is 100 percent dissociated into H^+ and HSO_4^- ions. The bisulfate ion, which dissociates according to the equation

$$HSO_4^- = H^+ + SO_4^{--} \tag{4}$$

behaves like a weak acid. Its dissociation constant is 1.26×10^{-2} and in a 0.1 molar H_2SO_4 solution the concentration of the SO_4^{--} is approximately .01 molar; i.e., about 10 percent of the HSO_4^- dissociates in sulfuric acid of this concentration. The bisulfate ion in a 0.1 molar solution of $NaHSO_4$, on the other hand, dissociates to the extent of about 30 percent. The dissociation of the HSO_4^- in sulfuric acid solution is less than that in a solution of $NaHSO_4$ of the same concentration because the excess H^+ has a common ion effect in the H_2SO_4 solution and represses the ionization of the HSO_4^-. There are no polybasic acids which are 100 percent dissociated in every step of the ionization.

Two common examples of dibasic acids which are weak in both stages of ionization are hydrogen sulfide, H_2S, and carbonic acid, H_2CO_3.

The first stage in the dissociation of hydrogen sulfide produces hydrogen and bisulfide ions.

$$H_2S = H^+ + HS^- \tag{5}$$

The HS^- formed in this reaction in turn dissociates to form hydrogen ion and sulfide ion.

$$HS^- = H^+ + S^{--} \tag{6}$$

The equilibrium expression for the first stage (equation 5) is

$$\frac{(H^+)(HS^-)}{(H_2S)} = K_1 = 1 \times 10^{-7} \tag{7}$$

and for the second stage,

$$\frac{(H^+)(S^{--})}{(HS^-)} = K_2 = 1.3 \times 10^{-13} \tag{8}$$

It will be observed that the constant for the second stage of ionization is almost 10^6 times smaller than that for the first stage; the HS^- ion is a very much weaker acid than is H_2S. The bisulfide ion is such a weak acid that of the amount formed by the dissociation of hydrogen sulfide only a very small fraction dissociates. For this reason, the concentrations of the H^+ and HS^- ions are practically equal to each other in a solution of pure hydrogen sulfide. The concentration of hydrogen sulfide in a solution saturated with the gas at 1 atmosphere pressure is very nearly 0.1 molar at room temperature, 25° C. With this information it is not difficult to calculate the concentration of both the hydrogen ion and the bisulfide ion in a solution saturated with hydrogen sulfide. Since only a very small fraction of the hydrogen sulfide dissociates we may consider the concentration of the undissociated portion of the hydrogen sulfide to be 0.1 molar (the amount which dissociates is negligible compared with 0.1). If we let X be the concentration of the hydrogen ion at equilibrium, X will also be the concentration of the bisulfide ion. We then have:

$$\frac{(H^+)(HS^-)}{(H_2S)} = \frac{X^2}{0.1} = 1 \times 10^{-7}$$

$$X^2 = 1 \times 10^{-8}$$

$$X = 1 \times 10^{-4} \text{ molar} = (H^+) = (HS^-)$$

If hydrogen ion is added to a saturated solution of hydrogen sulfide, the concentration of the undissociated hydrogen sulfide molecules will not be changed appreciably but the concentration of the bisulfide ion will be decreased and its concentration will be inversely proportional to the concentration of the hydrogen ion. The greater the concentration of the hydrogen ion, the smaller will be the concentration of the bisulfide ion.

A calculation of the concentration of the sulfide ion involves the second stage of ionization. For a saturated solution of hydrogen sulfide, we have just calculated the concentration of the hydrogen ion and of the bisulfide ion to be 1×10^{-4} molar. Since the dissociation constant for the second stage is so small,

only a very small amount of the bisulfide ion dissociates; that is, the second dissociation (equation 6) does not lower the concentration of the bisulfide ion appreciably. Its concentration may then be considered to be 1×10^{-4} molar even after the second stage of dissociation has been taken into account. Likewise, the amount of hydrogen ion produced by the second stage of ionization does not add appreciably to the hydrogen ion concentration produced by the dissociation of the H_2S. Hence we may take the final equilibrium value of the hydrogen ion concentration to be the same as that calculated for the first stage of ionization, namely 1×10^{-4} mole per liter. In other words, even after the second stage of ionization has been considered, the hydrogen ion and bisulfide ion concentrations are practically the same. We may then calculate the sulfide ion concentration:

$$\frac{(H^+)(S^{--})}{(HS^-)} = K_2 = 1.3 \times 10^{-13}$$

$$\frac{1 \times 10^{-4}(S^{--})}{1 \times 10^{-4}} = 1.3 \times 10^{-13}$$

$$(S^{--}) = 1.3 \times 10^{-13} \text{ mole per liter} \qquad (9)$$

Since the concentration of the hydrogen ion of the numerator in this expression cancels the bisulfide ion concentration of the denominator, the concentration of the sulfide ion is 1.3×10^{-13} molar. It will be noted that this value will be the approximate concentration of the sulfide ion even though the solution may not be saturated with hydrogen sulfide, for even under these conditions the concentration of the hydrogen ion and the concentration of the bisulfide ion will be practically equal to each other and will cancel in the equilibrium expression, leaving the sulfide ion concentration still 1.3×10^{-13} molar. In fact, for any weak polybasic acid the concentration of the doubly charged anion is practically equal to the second ionization constant.

The product of the equilibrium expressions for stages one and two of ionization (equations 7 and 8) is

$$\frac{(H^+)(HS^-)}{(H_2S)} \times \frac{(H^+)(S^{--})}{(HS^-)} = \frac{(H^+)^2(S^{--})}{(H_2S)} = K_1 \times K_2 = K_{12} \quad (10)$$

$$K_{12} = 1 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.3 \times 10^{-20}$$

or

$$\frac{(H^+)^2(S^{--})}{(H_2S)} = 1.3 \times 10^{-20} \quad (11)$$

This last expression cannot be used by itself to calculate both the concentration of the hydrogen ion and the sulfide ion in a solution which contains only hydrogen sulfide because both the concentration of the hydrogen ion and the concentration of the sulfide ion are unknown quantities and two equations are necessary to solve for two unknowns. The other equation necessary would involve K_1 alone. If the hydrogen ion concentration is determined from K_1 alone, then the sulfide ion concentration may be determined from equations (8) or (11).

Since a saturated solution of hydrogen sulfide in water is 0.1 molar with respect to the gas, we may write

$$\frac{(H^+)^2(S^{--})}{0.1} = 1.3 \times 10^{-20}$$

or

$$(H^+)^2(S^{--}) = 1.3 \times 10^{-21} = K_{12}(sat.) \quad (12)$$

Equation (12) may be used when the hydrogen ion concentration of the saturated solution of H_2S is known or calculated from equation (7).

When the hydrogen ion is added to the solution in the form of a strong acid then the sulfide ion concentration may be determined from equation (12), since the hydrogen ion concentration is now known from the amount of strong acid added; the amount produced by the dissociation of hydrogen sulfide is negligible. For example, suppose we wish to calculate the sulfide ion concentration in a saturated solution of hydrogen sulfide to which hydrochloric acid has been added to make the hydrogen ion concentration 0.1 molar. Applying equation (12), we have

$$(H^+)^2(S^{--}) = (0.1)^2(S^{--}) = 1.3 \times 10^{-21}$$

$$(S^{--}) = \frac{1.3 \times 10^{-21}}{.01} = 1.3 \times 10^{-19} \text{ molar}$$

In the same way we may calculate the sulfide ion concentration for solutions of any hydrogen ion concentration. The concentration of the sulfide ion is thus inversely proportional to the square of the hydrogen ion concentration. If the hydrogen ion concentration is increased tenfold over that in any given case, the sulfide ion concentration will accordingly be decreased one hundredfold. The following table gives the sulfide ion concentration for different solutions containing hydrogen sulfide. For the sake of completeness the table includes solutions of the sulfides for which calculations of the sulfide ion concentrations are considered in the next chapter on hydrolysis.

TABLE 23

CONCENTRATION OF THE SULFIDE ION IN DIFFERENT SOLUTIONS

Solution	(S^{--}) (Molar Concentrations)
0.1 molar H_2S	1.3×10^{-13}
0.1 molar H_2S and 0.001 molar H^+ ion	1.3×10^{-15}
0.1 molar H_2S and 0.01 molar H^+ ion	1.3×10^{-17}
0.1 molar H_2S and 0.1 molar H^+ ion	1.3×10^{-19}
0.1 molar H_2S and 1.0 molar H^+ ion	1.3×10^{-21}
0.1 molar $(NH_4)_2S$	2×10^{-5}
0.1 molar Na_2S	5×10^{-2}

Precipitation of the Sulfides. The concentration of the sulfide ion, in a solution saturated with hydrogen sulfide and which contains hydrogen ion in 1 molar concentration, has the exceedingly low value of about 1.3×10^{-21} mole per liter. Since there are 6×10^{23} molecules in one mole, 1.3×10^{-21} mole per liter corresponds to about 800 sulfide ions per liter — roughly, one ion per ml. (milliliter). Yet when this solution

is added to one containing .001 mole of copper ion, Cu^{++}, per liter, a black precipitate is formed immediately. It might seem inconceivable that such a small concentration of sulfide ions could cause this rapid precipitation of cupric sulfide, CuS, if the reaction mechanism were the simple combination between sulfide and cupric ions as represented by the equation,

$$Cu^{++} + S^{--} = CuS(solid) \qquad (13)$$

The concentration of the bisulfide ion in such a solution is very much larger than the concentration of the sulfide ion, and conceivably the bisulfide ion, HS^-, could combine with the cupric ions, and hydrogen sulfide would be liberated in such a way that the final result would be

$$2HS^- + Cu^{++} = CuS(solid) + H_2S \qquad (14)$$

In fact, it is not out of the question that an unstable intermediate compound, $Cu(HS)_2$, could be formed which immediately breaks down to form CuS and H_2S. Such processes are known in the formation of oxides by precipitation. For example, when a solution of silver nitrate is added to one of sodium hydroxide, there results a dark brown precipitate of silver oxide, Ag_2O. If the solutions used are dilute, a yellow-brown precipitate is first observed, very probably AgOH, and this changes to the brown precipitate of silver oxide with the loss of water,

$$2AgOH = Ag_2O + H_2O \qquad (15)$$

Likewise, cupric hydroxide, $Cu(OH)_2$, a blue precipitate formed by the addition of a sodium hydroxide solution to one containing cupric ion, such as a copper sulfate solution, slowly changes to black cupric oxide, CuO, when the precipitate is heated to 100° C.

$$Cu(OH)_2 = CuO + H_2O \qquad (16)$$

Sulfur and oxygen are in the same group in the periodic system, and hydrogen sulfide is therefore the analogue of water. Since hydrogen sulfide dissociates in two steps to give sulfide ions, so water undoubtedly does the same to give the

oxide ion, O^{--} ion, but since we have no means of measuring the oxide ion concentration, we have neglected it entirely. The oxide ion must be present at extremely low concentration, much lower than that of the sulfide ion in water solution. In view of these considerations it would not be surprising if we found that in the case of the precipitation of a sulfide the unstable hydrosulfide first formed and the breakdown of this to the sulfide and hydrogen sulfide then occurred.

The mechanism of the formation of a sulfide precipitate, or any precipitate for that matter, is immaterial in our calculations or reasoning involving the solubility product principle. We always assume that equilibrium is maintained, and when such is the case, the concentrations of the substances left in solution are those calculated by this principle, provided of course that the data upon which the calculations are based (solubility product constants) are correct. The precipitation of a given sulfide will take place for a given sulfide ion concentration even though this sulfide precipitate is not formed directly from its ions. The equilibrium involving a relatively insoluble salt in solution behaves as though the reaction takes place directly between its ions, regardless of what intermediate compounds may be formed. ***Equilibrium has to do only with the final result and not with the means by which the result is obtained.***

The Separation of Sulfides into Groups. If the concentration of the sulfide ion in a solution containing some metal ion, Me^{++}, is so small that the product, $(Me^{++})(S^{--})$, does not exceed the solubility product constant for the metallic sulfide, then no precipitate will be formed. On the other hand, if the sulfide ion concentration is such that this product exceeds the solubility product constant, then a precipitate will appear providing (1) that a supersaturated solution is not formed and (2) that the amount of the metallic ion in the solution is sufficiently great to give a visible effect. The largest concentration of hydrogen ion which can be used conveniently in analysis is about 1 molar. This concentration of hydrogen ion in a saturated solution of hydrogen sulfide, as we have seen (see

Table 23), provides a sulfide ion concentration of about 10^{-21} molar. It has been shown experimentally that sulfide precipitates are not visible if they are precipitated from solutions more dilute than 10^{-4} molar. This concentration is therefore taken as the limit of visibility of the precipitate. Therefore any sulfide of a bivalent metallic ion for which the solubility product constant is smaller than the product ($10^{-4} \times 10^{-21} = 10^{-25}$) should be precipitated in barely detectable amounts in a solution which is 1 molar in hydrogen ion. By referring to the table of solubility product constants for some of the sulfides given in the Appendix, it will be observed that the sulfides of cadmium, copper, lead and mercury are included in this group. Other sulfides with greater solubility product constants require a greater sulfide ion concentration, hence a smaller hydrogen ion concentration, to bring about precipitation.

The sulfides are then divided into two groups, (1) those which precipitate in acid solution and (2) those which precipitate in solutions of low hydrogen ion concentration. In practice one group is often precipitated in acid solution and filtered, the other group is precipitated by hydrogen sulfide after neutralizing the solution and making it alkaline. This last procedure then increases the sulfide ion concentration sufficiently to precipitate all sulfides that were not precipitated in the acid solution.

In practically all cases the precipitation of a metallic sulfide requires a much smaller H^+ ion concentration (larger S^{--} ion concentration) than is necessary to dissolve the already precipitated sulfide. This may be explained on the basis that crystal nuclei of the sulfides are not present in the solution and that higher concentrations of S^{--} ion are necessary to form them. Once these have been formed the precipitation takes place rapidly. In the case of some sulfides, notably NiS, CoS, and ZnS, the freshly precipitated sulfide is not in the form of perfect crystals — somewhat amorphous. This freshly precipitated form of the sulfide is less stable than the crystalline form. However, there is good evidence to indicate that the freshly

precipitated form rapidly rearranges to the more stable crystalline form and therefore becomes less soluble in acid solution. The solubility product therefore varies with time. For some purposes we need to know the solubility product of the most stable form. However, for purposes of qualitative analysis we should like to know the solubility product of the freshly precipitated form, for it is with that form that we are dealing. The solubility product constants given in Tables in the Appendix, wherever data are available, are those of the freshly precipitated product. The solubility products of the sulfides are less reliable than those of other relatively insoluble precipitates.

The Precipitation of Ferrous and Zinc Sulfides. If acetic acid is added to a solution which is 0.1 molar with respect to both ferrous, Fe^{++}, and zinc, Zn^{++}, ions, until its concentration is approximately 0.1 molar, and then hydrogen sulfide is passed into this solution, a white precipitate of zinc sulfide will be formed. Under these conditions ferrous sulfide, FeS, which is black, is not precipitated. The hydrogen ion concentration of a 0.1 *M* acetic acid solution is approximately 10^{-3} *M*. From equation (12) we calculate the sulfide ion concentration to be about 10^{-15} *M*. Since precipitation occurs we may now conclude that the solubility product constant for zinc sulfide, ZnS, is less than $10^{-1} \times 10^{-15}$ or 10^{-16}. Since the ferrous sulfide does not precipitate under these conditions we might conclude that the solubility product constant for ferrous sulfide is greater than 10^{-16}. However, we should not be entirely justified in this conclusion for (1) a supersaturated solution may form and (2) the solubility product is different for the first formed small crystals. The value given in the tables is usually determined for large crystals. As a matter of fact, the solubility product constant given in the tables (see the Appendix) for ferrous sulfide (4×10^{-17}) is slightly smaller than 10^{-16}. The data from which we made our calculation may be in error by this small amount (a factor of about two or so) or the effects of supersaturation and small crystals may play a significant rôle here.

If sodium acetate is added to the solution considered above,

a black precipitate of the ferrous sulfide is obtained. The effect of the addition of sodium acetate is to lower the concentration of the hydrogen ion through the formation of the weak acetic acid.

$$H^+ + Ac^- = HAc$$

Lowering the hydrogen ion concentration raises the sulfide ion concentration to a point sufficient to cause the precipitation of ferrous sulfide. The same result could have been achieved by the addition of either sodium hydroxide or ammonium hydroxide. The hydroxide ion is even more effective than the acetate ion in reducing the hydrogen ion concentration.

When any metallic sulfide is precipitated with hydrogen sulfide the hydrogen ion concentration in the solution is increased during the course of the reaction.

$$H_2S + Me^{++} = MeS_{(s)}* + 2H^+ \qquad (17)$$

This increase in hydrogen ion concentration may become great enough to render the precipitation incomplete. However, if hydroxide ion, acetate ion, ammonium hydroxide, or any ion or molecule which combines with hydrogen ion, is present in the solution the reaction proceeds readily with the formation of the sulfide, MeS.

While a 10^{-4} molar solution of the metallic ion is the approximate limit of visibility of a precipitate, yet this is not the lower limit of concentration which will discolor some other precipitate which might be formed. For example, if zinc sulfide, which when pure is white, is precipitated from a solution which contains only a slight trace of ferrous ion, the resulting precipitate will be gray. In fact, zinc sulfide seldom appears pure white when other ions are also in the solution. The small amount of ferrous sulfide which gives rise to the gray color may be prevented from precipitating by dissolving the gray precipitate in acetic acid and diluting to about 0.1 molar and again adding hydrogen sulfide. The presence of the hydrogen ions from the acetic acid lowers the sulfide ion concentration

* (*s*) is used to denote a solid phase.

to a value which will prevent the formation of ferrous sulfide and the zinc sulfide will now appear white.

The precipitation of zinc sulfide and ferrous sulfide have been discussed here in order to show the important rôle that the hydrogen ion concentration plays in the precipitation of sulfides. The solubility product constants of copper and mercuric sulfides are so small that the hydrogen ion concentration cannot be increased sufficiently to prevent precipitation. Any sulfide which precipitates from acid solutions will of course precipitate from alkaline solutions for which the hydrogen ion concentration has a smaller, and the sulfide ion concentration a larger value.

Carbonic Acid and the Precipitation of the Carbonates. The ionization of carbonic acid in two steps is entirely analogous to the ionization of hydrogen sulfide. These two steps are represented by the equations:

$$H_2CO_3 = H^+ + HCO_3^- \tag{18}$$

and

$$HCO_3^- = H^+ + CO_3^{--} \tag{19}$$

The bicarbonate ion, like the bisulfide ion, is a very much weaker acid than the acid from which it is derived. The dissociation constants for carbonic acid, however, are somewhat larger than the similar constants for hydrogen sulfide.

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = 4.2 \times 10^{-7} \tag{20}$$

and

$$\frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = 4.8 \times 10^{-11} \tag{21}$$

By multiplying equation (20) by equation (21), we obtain

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \times \frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = \frac{(H^+)^2(CO_3^{--})}{(H_2CO_3)}$$

$$= 4.2 \times 10^{-7} \times 4.8 \times 10^{-11}$$

Therefore,

$$\frac{(H^+)^2(CO_3^{--})}{(H_2CO_3)} = 2 \times 10^{-17} \tag{22}$$

A saturated solution of carbon dioxide in water at 1 atmosphere pressure and at 25° C contains about .034 mole per liter. Since in this solution such a small fraction of the acid dissociates, the undissociated portion is present at very nearly the same concentration, i.e., .034 molar. Since the second stage of ionization occurs to an extremely small extent, it may be neglected in calculating the concentration of the hydrogen ion or the concentration of the bicarbonate ion. If X is the concentration of each of these ions then, according to equation (20),

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)} = \frac{X^2}{.034} = 4.2 \times 10^{-7}$$

$$X^2 = 14.3 \times 10^{-9} = 1.43 \times 10^{-8}$$

$$X = 1.2 \times 10^{-4} \text{ mole per liter} = (H^+) = (HCO_3^-)$$

In calculating the carbonate ion concentration in such a solution from equation (21), we observe that since the hydrogen ion and bicarbonate ion concentrations are very nearly the same, they cancel in this expression and the carbonate ion concentration is equal in value to the second ionization constant, namely, 4.8×10^{-11} mole per liter.

The insoluble carbonates differ markedly from the sulfides in the magnitude of their solubility product constants; the solubility product constants for the most soluble of the so-called insoluble sulfides are considerably smaller in magnitude than those for the least soluble of the carbonates. Whereas most of the sulfides can be precipitated by the addition of hydrogen sulfide to solutions of their salts, this is not the case for any of the carbonates. They cannot be precipitated by the direct addition of carbon dioxide gas to solutions containing the appropriate metal ions. The product of the concentrations of the carbonate ion and the metal ion in such solutions is not larger than the solubility product constants of the respective carbonates. From an inspection of the values of the solubility product constant of lead carbonate it might appear that it could be precipitated from a solution containing lead ions by

the direct addition of carbon dioxide gas, but the salts of this metal hydrolyze (subject to be considered in the next chapter) sufficiently to give an appreciable hydrogen ion concentration, which in turn lowers the carbonate ion concentration. Just as in the case of hydrogen sulfide where an increase in the hydrogen ion concentration is accompanied by a decrease in the sulfide ion concentration, so in this case increasing the hydrogen ion concentration decreases the carbonate ion concentration.

The insoluble carbonates can then be precipitated only when the carbonate ion concentration is increased. This may be easily brought about by lowering the hydrogen ion concentration through the addition of a base. As a matter of fact, carbonic acid is not used for the precipitation of the carbonates but rather solutions of soluble carbonates such as sodium carbonate or ammonium carbonate, in which the concentration of the carbonate ion is relatively high. In qualitative analytical procedures these soluble carbonates are used to precipitate $CaCO_3$, $SrCO_3$, and $BaCO_3$.

Examples of Problems Involving Polybasic Acids and Sulfide Precipitation

Example 1.

Calculate the CO_3^{--} concentration in a solution which is 0.1 molar in HCl and saturated with CO_2 at 1 atmosphere. In this solution the solubility is practically the same as that in water, namely .034 molar.

Since HCl is a strong acid the H^+ concentration is 0.1 M. The increase in the concentration of this ion, because of the dissociation of H_2CO_3, is negligibly small and may be left out of consideration.

$$\frac{(H^+)^2(CO_3^{--})}{(H_2CO_3)} = 2 \times 10^{-17}$$

$$\frac{(0.1)^2(CO_3^{--})}{.034} = 2 \times 10^{-17}$$

$$(CO_3^{--}) = \frac{.034 \times 2 \times 10^{-17}}{10^{-2}} = 6.8 \times 10^{-17}\ M$$

Example 2.

Calculate the (H^+) necessary to give a (S^{--}) of 1×10^{-18} molar in a saturated solution of hydrogen sulfide. H_2S is soluble to the extent of 0.1 *M*.

$$\frac{(H^+)^2(S^{--})}{(H_2S)} = 1.3 \times 10^{-20}$$

$$\frac{(H^+)^2 \times 1 \times 10^{-18}}{0.1} = 1.3 \times 10^{-20}$$

$$(H^+)^2 = 1.3 \times 10^{-3} = 13 \times 10^{-4}$$

$$(H^+) = 3.6 \times 10^{-2}\ M$$

Example 3.

Calculate the minimum (H^+) necessary to prevent precipitation of ZnS when a .01 *M* $ZnCl_2$ solution is saturated with H_2S. The $K_{S.P.}$ for ZnS = 1×10^{-20}.

The (S^{--}) below which no precipitation of ZnS takes place can be calculated from the solubility product constant.

$$(Zn^{++})(S^{--}) = .01 \times (S^{--}) = 1 \times 10^{-20}.$$

$$(S^{--}) = 1 \times 10^{-18}$$

The (H^+) which will be in equilibrium with this (S^{--}) may be obtained from the expression

$$\frac{(H^+)^2(S^{--})}{(H_2S)} = \frac{(H^+)^2 \times 1 \times 10^{-18}}{0.1} = 1.3 \times 10^{-20}$$

$$(H^+)^2 = 1.3 \times 10^{-3} = 13 \times 10^{-4}$$

$$(H^+) = 3.6 \times 10^{-2} = .036\ M$$

Note: This answer should be regarded as only an approximation, inasmuch as the solubility product for freshly precipitated ZnS, like that of many sulfides, is not accurately known.

Example 4.

A solution contains .02 mole of Cd^{++} ion, .02 mole of Zn^{++} ion, and 1 mole of HCl per liter, and is saturated with H_2S at room temperature.

(a) What is the concentration of the S^{--} ion in this solution?

(b) Will CdS precipitate?

(c) Will ZnS precipitate?

Since the solubility of H_2S in the solution is 0.1 *M* then we may write

$$\frac{(H^+)^2(S^{--})}{(H_2S)} = \frac{(H^+)^2(S^{--})}{0.1} = 1.3 \times 10^{-20}$$

or $$(H^+)^2(S^{--}) = 1.3 \times 10^{-21}$$

If the (H^+) is 1 *M*, then

$$(1)^2(S^{--}) = 1.3 \times 10^{-21} \quad \text{and} \quad (S^{--}) = 1.3 \times 10^{-21}$$

If precipitation of both sulfides takes place, then at equilibrium the reactions are

$$CdS_{(s)} = Cd^{++} + S^{--}$$
$$ZnS_{(s)} = Zn^{++} + S^{--}$$

The solubility product expressions are respectively

$$(Cd^{++})(S^{--}) = 6 \times 10^{-27}$$
$$(Zn^{++})(S^{--}) = 1 \times 10^{-20}$$

In the case of CdS, the ion product, $(.02)(1.3 \times 10^{-21}) = 2.6 \times 10^{-23}$, is greater than the solubility product constant, so CdS precipitates. On the other hand, the ion product for ZnS, 2.6×10^{-23}, is less than the solubility product constant, so ZnS does not precipitate.

Example 5.

Calculate the concentration of the PO_4^{---} ion in a 0.1 *M* solution of H_3PO_4.

The H_3PO_4 ionizes in three stages, as follows:

$$H_3PO_4 = H^+ + H_2PO_4^- \quad (1)$$
$$H_2PO_4^- = H^+ + HPO_4^{--} \quad (2)$$
$$HPO_4^{--} = H^+ + PO_4^{---} \quad (3)$$

The equilibrium expressions for the three stages of ionization are respectively

$$\frac{(H^+)(H_2PO_4^-)}{(H_3PO_4)} = K_{I_1} = 7.5 \times 10^{-3}$$

$$\frac{(H^+)(HPO_4^{--})}{(H_2PO_4^-)} = K_{I_2} = 6.2 \times 10^{-8}$$

$$\frac{(H^+)(PO_4^{---})}{(HPO_4^{--})} = K_{I_3} = 1 \times 10^{-12}$$

First calculate (H^+) and $(H_2PO_4^-)$ from the first stage of ionization.

$$H_3PO_4 = H^+ + H_2PO_4^-$$

Concentrations: $0.1 - X \quad X \quad X$

Therefore $$\frac{(H^+)(H_2PO_4^-)}{(H_3PO_4)} = \frac{X^2}{0.1 - X} = 7.5 \times 10^{-3}$$

Since the ionization constant is relatively large, X cannot be neglected in the denominator. Therefore

$$X^2 = 7.5 \times 10^{-3}\,(0.1 - X) = 7.5 \times 10^{-4} - 7.5 \times 10^{-3}\,X$$

or $$X^2 + 7.5 \times 10^{-3}\,X - 7.5 \times 10^{-4} = 0$$

Solution of the quadratic equation (see Appendix) gives $X = 2.4 \times 10^{-2}\,M = (H^+) = (H_2PO_4^-)$

Now calculate the (HPO_4^{--}) from the second stage of ionization.

$$H_2PO_4^- = H^+ + HPO_4^{--}$$

Concentrations: $(2.4 \times 10^{-2} - X) \quad (2.4 \times 10^{-2} + X) \quad X$

Therefore

$$\frac{(H^+)(HPO_4^{--})}{(H_2PO_4^-)} = \frac{(2.4 \times 10^{-2} + X)(X)}{(2.4 \times 10^{-2} - X)} = 6.2 \times 10^{-8}$$

Since the ionization constant is small, the value of X is negligible as compared with 2.4×10^{-2}; consequently, X may be neglected when it is subtracted from or added to this number. Then

$$X = (HPO_4^{--}) = 6.2 \times 10^{-8}\,M$$

Finally calculate (PO_4^{---}) from the third stage of ionization.

$$HPO_4^{--} = H^+ + PO_4^{---}$$

Concentrations: $(6.2 \times 10^{-8} - X) \quad (2.4 \times 10^{-2} + X) \quad X$

Therefore

$$\frac{(H^+)(PO_4^{---})}{(HPO_4^{--})} = \frac{(2.4 \times 10^{-2} + X)(X)}{(6.2 \times 10^{-8} - X)} = 1 \times 10^{-12}$$

Again neglecting X in comparison with 2.4×10^{-2} and with 6.2×10^{-8} on the basis of the extremely small value of the ionization constant (1×10^{-12}), the expression becomes

$$\frac{(2.4 \times 10^{-2})(X)}{(6.2 \times 10^{-8})} = 1 \times 10^{-12}$$

$$X = \frac{(1 \times 10^{-12})(6.2 \times 10^{-8})}{(2.4 \times 10^{-2})} = 2.6 \times 10^{-18}$$

Therefore $X = (PO_4^{---}) \approx 2.6 \times 10^{-18}\ M$. The concentration of the PO_4^{---} ion in a 0.1 M solution of H_3PO_4 is approximately $10^{-18}\ M$.

Example 6.

To 50 ml. of 0.11 M $CdSO_4$ solution is added 5 ml. of 3 M HCl solution. The mixture is then saturated with H_2S at room temperature and CdS is found to precipitate. What is the concentration of the Cd^{++} ion left in solution? (Do not neglect the (H^+) produced by the reaction.)

Before precipitation the (Cd^{++}) has a value of $\frac{50}{55} \times 0.11$ or 0.1 M. The (H^+) is $\frac{5}{55} \times 3$ or 0.28 M. The reaction which takes place as the CdS precipitates is

$$Cd^{++} + H_2S = CdS_{(s)} + 2H^+$$

Since the reaction proceeds practically to completion, the increase in the (H^+) during the course of the reaction is 0.2 M. Thus, the total (H^+) in the solution when equilibrium is reached is 0.28 M + 0.2 M or 0.48 M. In a solution of this (H^+), saturated with H_2S, the (S^{--}) is

$$(H^+)^2(S^{--}) = 1.3 \times 10^{-21}$$
$$(0.48)^2(S^{--}) = 1.3 \times 10^{-21}$$
$$(S^{--}) = 5.6 \times 10^{-21}$$

Since the Cd^{++} ion is in equilibrium with the S^{--} ion,

$$(Cd^{++})(S^{--}) = K_{S.P.} = 6 \times 10^{-27}$$
$$(Cd^{++})(5.6 \times 10^{-21}) = 6 \times 10^{-27}$$
$$(Cd^{++}) = 1.1 \times 10^{-6}\ M$$

Therefore, the (Cd^{++}) left in solution is 1.1×10^{-6} mole per liter.

Questions and Problems

1. Sulfuric acid is usually regarded as a strong acid. In what respect could it be placed in the category of weak acids?
2. Explain without calculation why zinc sulfide cannot be precipitated from a solution which is 1 molar with respect to H^+ while copper sulfide can.
3. Is it necessary that we know the mechanism or steps by which a

given reaction takes place in order to apply the Law of Mass Action to an equilibrium involving this reaction?

4. How could you precipitate ZnS from a solution containing Zn^{++} and Fe^{++} without precipitating FeS?
5. Why cannot insoluble carbonates be precipitated from solution by CO_2 or H_2CO_3 in a way that is analogous to the precipitation of the sulfides by H_2S?
6. Explain why it is not possible to precipitate slightly soluble phosphates from solution with phosphoric acid.
7. Explain why $BaCO_3$ dissolves in dilute HCl solution while $BaSO_4$ does not.
8. What is the concentration of the $C_2O_4^{--}$ ion in a 0.1 *M* $H_2C_2O_4$ solution? Will such a solution precipitate MgC_2O_4 if $MgCl_2$ is added to make the solution 0.1 *M* with respect to Mg^{++} ion? (Note: in the $H_2C_2O_4$ solution the concentration of the H^+ ion is practically the same as that for the $HC_2O_4^-$ ion.)
9. What is the concentration of the S^{--} ion in a solution saturated with H_2S at one-half atmosphere pressure and room temperature? What is the concentration of the H^+ ion in this solution? (The solubility of a gas is proportional to the saturation pressure — Henry's Law.)
10. What is the H^+ concentration in a water solution of H_2CO_3 saturated with CO_2 at a pressure of 500 lb. per square inch (34 atmospheres)? (A solution saturated with CO_2 at 1 atmosphere pressure at the same temperature contains .034 mole CO_2 per liter. Assume Henry's Law applies.)
11. Calculate the concentration of the H^+ ion in the following solutions. Neglect all but the first step of ionization.
    (a) 0.1 *M* H_2CO_3
    (b) 0.01 *M* H_2CO_3
    (c) 0.01 *M* H_2S
    (d) 0.04 *M* H_3BO_3
    (e) 0.2 *M* $ClCH_2COOH$
    (f) 0.1 *M* H_3PO_4
    (g) 0.1 *M* $H_2C_2O_4$
12. Solutions of HCl are saturated with H_2S. From the total H^+ ion concentrations given below, calculate the corresponding S^{--} ion concentrations.

H^+ concentration	
(a) 1×10^{-4} *M*	(d) 1×10^{-1} *M*
(b) 1×10^{-3} *M*	(e) 1 *M*
(c) 1×10^{-2} *M*	

13. Plot the results of problem (12) using (H^+) as ordinates and (S^{--}) as abscissae. It may be convenient to save this plot for future reference.

14. Five ml. of 6 *M* HCl is added to 95 ml. of a solution containing 1 g. $ZnSO_4$ and 1 g. $CdSO_4$, and the solution is saturated with H_2S at room temperature.

(a) What is the concentration of the H^+ ion before H_2S is introduced?

(b) What is the concentration of the S^{--} ion after the solution becomes saturated with H_2S?

(c) Will CdS precipitate?

(d) Will ZnS precipitate?

(e) Explain your conclusions in detail.

15. Hydrogen sulfide is gradually added to a neutral solution which is 0.1 *M* in Cd^{++} ion and 0.1 *M* in Zn^{++} ion. Calculate the concentration of the Cd^{++} ion when ZnS begins to precipitate.

16. To 100 ml. of a hot .03 *M* solution of $PbCl_2$ is added 5 ml. of 6 *M* HCl solution. When the resulting solution is saturated with H_2S, PbS precipitates. How many moles of Pb^{++} ion are left in solution after it has cooled to room temperature? (Do not neglect the H^+ ion produced by the reaction.)

17. Hydrogen sulfide is added to separate solutions containing 50 mg each of the following positive ions in 1 liter of solution. What is the S^{--} ion concentration when precipitation begins?

(a) Cu^{++} (b) Pb^{++} (c) Zn^{++} (d) Hg^{++} (e) Cd^{++}

18. A quantitative determination of zinc as ZnS is to be made. What must be the maximum concentration of the H^+ ion in the solution if no more than 0.3 mg. of Zn^{++} ion is to be left in a 100 ml. sample of the solution when saturated with H_2S?

19. Calculate the S^{--} ion concentration in a 0.1 *M* acetic acid solution which is saturated with H_2S.

20. Calculate the approximate concentrations of the following ions in a .05 *M* solution of phosphoric acid.

(a) H^+ (b) $H_2PO_4^-$ (c) HPO_4^{--} (d) PO_4^{---}

21. Ten ml. of 3 *M* HCl is added to 200 ml. of a solution containing .05 mole of $CuSO_4$ and .05 mole of $CdSO_4$, and the solution is saturated with H_2S at room temperature. Both CuS and CdS precipitate. How many moles of Cu^{++} ion and of Cd^{++} ion are

left in solution? (Do not neglect the H^+ ion produced by the reactions.)

22. What must be the minimum concentration of a HCl solution to dissolve .01 mole of freshly precipitated ZnS in a liter of the solution?

23. What must be the minimum concentration of a HCl solution to dissolve .01 mole of CuS in a liter of the solution? Would it be possible to dissolve the CuS under these conditions?

24. One-tenth mole of Na_2SO_4 and 0.1 mole $NaHSO_4$ are added to enough water to make 100 ml. of solution. What is the H^+ ion concentration in this solution? HSO_4^- ion is a weak acid with a dissociation constant equal to .0126

This solution is then made .02 *M* with respect to each of the ions, Zn^{++}, Co^{++}, and Ni^{++}. It is then saturated with H_2S. Show by calculation that all three sulfides should precipitate. In practice only ZnS precipitates under these conditions. This is due to the fact that the rate of precipitation of ZnS is rapid whereas the rate of precipitation of CoS and of NiS is too slow under these conditions.

CHAPTER

10

The Ionization of Water — Hydrolysis

The Equilibrium between Water and Its Ions. Water is often regarded as a non-conductor of electricity. When the instruments used in measuring conductance are not exceedingly sensitive and when the voltage used is not exceedingly high, pure water shows no appreciable conductance. Very sensitive instruments, however, show that pure water actually does conduct electricity to a very small extent. This conductance is due to the dissociation of a very small fraction of the water molecules into hydrogen and hydroxide ions, and in pure water the concentrations of these ions must be identical. Therefore, water may be regarded both as an acid and as a base.

Since water is the medium in which all electrolytes are dissociated and since water solutions are by far the most commonly occurring solutions in chemistry, the equilibrium between water and its ions is one of the greatest importance in all phases of chemistry that deal with solutions, not only in qualitative analysis but particularly in the chemistry of all plant and animal systems.

The reaction representing the equilibrium between water and its ions is

$$H_2O = H^+ + OH^- \qquad (1)$$

If we followed the previously discussed rule regarding equilibrium constants, we would write the equilibrium expression for the reaction

$$\frac{(H^+)(OH^-)}{(H_2O)} = K$$

But the concentration of the hydrogen and hydroxide ions is so small in comparison with the large concentration of undissociated molecules that, for all practical purposes, the concentration of the undissociated molecules (denominator of above expression) may be regarded as a constant. One liter of water contains 55.5, i.e., $\frac{1000}{18}$, moles of water, and if this concentration should vary as much as 0.1 of a mole in any given reaction, the change in the concentration of the water molecules, (H_2O), would be negligible. Suppose, for example, that 0.1 mole of water was used up by some reaction which also involved this equilibrium. The amount of water left in the original 1 liter of solution, after the reaction was completed, would now be 55.4 moles instead of 55.5 moles. The difference between these two values is less than 0.2 percent and for all practical purposes we may regard the concentration of the undissociated water molecules as not having changed, i.e., (H_2O) is constant.

We may, therefore, write

$$(H^+)(OH^-) = K(H_2O)$$
$$(H^+)(OH^-) = K \times \text{constant}$$
$$(H^+)(OH^-) = K_w \qquad (2)$$

where $K_w = K \times \text{constant} = K(H_2O)$. K_w is known as the dissociation constant of water. It has a value of 1×10^{-14} at room temperature. This means that for pure water

$$(H^+)(OH^-) = 1 \times 10^{-14}$$

and

$$(H^+) = (OH^-) = 1 \times 10^{-7} \text{ mole per liter}$$

The equilibrium existing between water and its ions (not the value of the equilibrium constant) can be shifted or changed

(1) by the addition of hydroxide ions in the form of a base or by the addition of hydrogen ions in the form of an acid, or

(2) by the removal of hydrogen ions or hydroxide ions through the addition of some other substance.

Let us consider the equilibrium between water and its ions

(equation 1) and reiterate what is meant by the shifting of an equilibrium. By increasing the concentration of any of the substances on the right side of the equation, hydrogen ion or hydroxide ion, the equilibrium is shifted to the left. The equilibrium cannot be shifted to the right by increasing the concentration of the substance on the left for there is no way in which we can increase the concentration of water. The water molecules are already as close together as it is possible for them to be. By decreasing the concentration of either the hydrogen ion or the hydroxide ion, however, the equilibrium is shifted to the right.

Suppose some sodium hydroxide is added to pure water. This increases the concentration of the hydroxide ion with the final result that the hydrogen and hydroxide ions are still in equilibrium with each other, but the conditions of equilibrium are not the same as those existing in pure water. Strictly speaking, we should not say that the equilibrium is changed, for in the end condition there is still an equilibrium involving the same substances and the value of the equilibrium constant remains the same, but the *conditions* of equilibrium are changed. During the change in the conditions of equilibrium it is necessary that the concentration of the hydrogen ion decrease because the concentration of the hydroxide ion increases. The only way that the concentration of the hydrogen ion can decrease is by the combination of the hydrogen ions with some of the hydroxide ions to form water. In other words, the equilibrium under these conditions is said to shift from right to left to establish the new conditions; i.e., referring to equation (1), the reaction that re-establishes equilibrium is that proceeding from right to left. The original concentrations of the hydrogen and hydroxide ions were each 10^{-7} molar before the extra hydroxide ions were introduced. If the final concentration of the hydroxide ions, after equilibrium was re-established, was 10^{-5} molar, i.e., 100 times larger, then the final concentration of the hydrogen ion must be 10^{-9} molar or 100 times smaller than originally. Thus, under these new conditions,

$$(H^+)(OH^-) = 10^{-9} \times 10^{-5} = 10^{-14}$$

The concentration of the hydrogen ion is always inversely proportional to the concentration of the hydroxide ion. If one is increased tenfold, the other *must* be decreased tenfold; if one is increased fiftyfold, the other *must* be decreased fiftyfold of the original concentration. In no case does the concentration of either the hydroxide ion or the hydrogen ion become zero, because the Law of Mass Action would then require the concentration of the other ion to be infinite. The concentration of the hydrogen ion in a 1 molar solution of sodium hydroxide is about 10^{-14} molar. Likewise, the concentration of the hydroxide ion in a .01 molar solution of hydrochloric acid is 10^{-12} molar.

In the process of removing one of the ions of water by the addition of some other substance, new conditions of equilibrium are established by the dissociation of water to produce more ions and the equilibrium is shifted to the right (equation 1). It is with this process of partial removal of one of the ions of water that we are concerned in the problem of *hydrolysis.*

Hydrolysis. To understand better the process of hydrolysis let us consider this same equilibrium from a kinetic standpoint; i.e., from the standpoint of the motions of the molecules. In the equilibrium

$$H_2O = H^+ + OH^-$$

we may regard the reaction proceeding from left to right, as taking place through collisions of water molecules with each other. In the reverse reaction it is necessary that hydrogen ions and hydroxide ions collide with each other to react and form water molecules. At equilibrium both processes are proceeding at the same rate; as much water forms as dissociates. Now if it were possible to capture and remove a large part of the hydrogen ions as fast as they are formed, how would this equilibrium be affected? Water molecules would continue to dissociate at the same rate as they did previously, and since under these conditions the hydroxide ions could find fewer

hydrogen ions, the reverse reaction would be temporarily blocked and the hydroxide ions would accumulate and increase in concentration.

There are substances which capture hydrogen ions and thereby cause an increase in the hydroxide ion concentration. The negative ion of any weak acid is a captor of hydrogen ions since a weak acid is formed. This process of capture does not go on indefinitely, for evidently the weak acid will itself dissociate to some extent to give hydrogen ions and a negative ion, eventually feeding hydrogen ions back into the medium at the same rate at which they are removed. The net result is that some hydrogen ions are removed and the number of hydroxide ions is increased.

This is the process taking place in hydrolysis. Let us consider a specific case, that of adding sodium acetate to water. The acetate ions, Ac^-, from sodium acetate capture some of the hydrogen ions from water to form weak acetic acid molecules.

$$H_2O \rightleftharpoons \boxed{\begin{array}{c} H^+ \\ + \\ Ac^- \end{array}} + OH^-$$

$$\downarrow\uparrow$$

$$HAc$$

The acetic acid molecules dissociate to give back hydrogen ions, but a great number have been effectively removed from the medium and as a consequence the concentration of the hydroxide ion is increased. Another way of expressing this is: when acetate ions are added to the solution both acetate and hydroxide ions are competing for the hydrogen ions and therefore the concentration of the hydrogen ion is lowered. Reasoning on the basis of the equilibrium expression for water, the hydroxide ion concentration must be increased if the hydrogen ion concentration is decreased.

Similarly, the hydroxide ion may be captured, thereby increasing the concentration of the hydrogen ion. Ammonium

ion, NH_4^+, is a captor of hydroxide ions. Any salt of ammonium hydroxide, such as ammonium chloride, ammonium sulfate, or ammonium nitrate, when added to water, will hydrolyze to produce a small amount of NH_4OH and give an acid solution. It follows then that salts of weak acids and strong bases give alkaline solutions (OH^- ions in excess) and salts of strong acids and weak bases give acid solutions (H^+ ions in excess).

Salts of strong acids and strong bases do not hydrolyze. The ions of these salts do not have the ability to capture either hydrogen ions or hydroxide ions. To illustrate this point let us consider a solution of sodium chloride which is a salt of a strong acid (HCl) and a strong base (NaOH). In this solution neither the sodium ion nor the chloride ion has any tendency to capture either the hydrogen ion or the hydroxide ion, for both HCl and NaOH in solution are 100-percent ionized.

The salts of weak acids and weak bases hydrolyze to a relatively large extent, capturing both the hydrogen ion and the hydroxide ion, and their solutions will be either basic or acidic depending upon which is the weaker, the acid or the base formed in the hydrolysis process. For example, a solution of ammonium cyanide, NH_4CN, will give an alkaline reaction because hydrocyanic acid, HCN, is weaker as an acid than is ammonium hydroxide as a base; that is, HCN tends to hold the hydrogen ions more tightly than NH_4OH holds the hydroxide ions.

We may write the reaction occurring during the hydrolysis of sodium acetate as follows:

$$Ac^- + H_2O = HAc + OH^- \qquad (3)$$

The reaction proceeding from left to right is that which represents the capture of hydrogen ions by acetate ions. It is to be noted that this equation represents the over-all reaction. By this we mean that it tells us only what disappears and what is formed regardless of the intermediate steps. The reaction for hydrolysis is *not*, as one might expect,

$$H^+ + Ac^- = HAc$$

even though the water might first dissociate to give hydrogen ion. It is only one step of the hydrolysis reaction. In the overall process water molecules and acetate ions ultimately disappear while hydroxide ions and acetic acid molecules are formed.

The equilibrium expression for reaction (3) is

$$\frac{(\mathrm{HAc})(\mathrm{OH^-})}{(\mathrm{Ac^-})} = K_{\mathrm{H}} \tag{4}$$

As in the case of the equilibrium expression for water, the concentration of the water molecules, (H_2O), does not vary appreciably and is therefore omitted from the denominator of this expression. We may obtain the value of K_{H} from the values for the ionization constants of water and of acetic acid, the only two weak substances involved in the equilibrium. In every aqueous solution the H^+ and OH^- ions are in equilibrium with each other and

$$(\mathrm{H^+})(\mathrm{OH^-}) = K_{\mathrm{W}} \quad \text{or} \quad (\mathrm{OH^-}) = \frac{K_{\mathrm{W}}}{(\mathrm{H^+})}$$

Substituting $\frac{K_{\mathrm{W}}}{(\mathrm{H^+})}$ for (OH^-) in equation (4), we obtain

$$\frac{(\mathrm{HAc})K_{\mathrm{W}}}{(\mathrm{Ac^-})(\mathrm{H^+})} = K_{\mathrm{H}}$$

But $\frac{(\mathrm{HAc})}{(\mathrm{Ac^-})(\mathrm{H^+})}$ is equal to $\frac{1}{K_{\mathrm{A}}}$. Therefore

$$\frac{K_{\mathrm{W}}}{K_{\mathrm{A}}} = K_{\mathrm{H}} = \frac{1 \times 10^{-14}}{1.85 \times 10^{-5}} = 5.4 \times 10^{-10} \tag{5}$$

We may verify this relationship in the following way

$$\frac{K_{\mathrm{W}}}{K_{\mathrm{A}}} = \frac{(\mathrm{H^+})(\mathrm{OH^-})}{\dfrac{(\mathrm{H^+})(\mathrm{Ac^-})}{(\mathrm{HAc})}} = \frac{(\mathrm{HAc})(\mathrm{H^+})(\mathrm{OH^-})}{(\mathrm{H^+})(\mathrm{Ac^-})} = \frac{(\mathrm{HAc})(\mathrm{OH^-})}{(\mathrm{Ac^-})} = K_{\mathrm{H}}$$

Similarly, the equilibrium expression for the hydrolysis of an ammonium salt,

$$NH_4^+ + H_2O = NH_4OH + H^+ \tag{6}$$

becomes

$$\frac{(H^+)(NH_4OH)}{(NH_4^+)} = K_H \tag{7}$$

Substituting $\frac{K_W}{(OH^-)}$ for (H^+) in equation (7) we obtain

$$K_H = \frac{K_W}{K_I \text{ (for the base)}} \tag{8}$$

A salt of a weak acid and a weak base hydrolyzes to a large extent. This is to be expected since both H^+ and OH^- ions are captured by the negative and positive ions of the salt. Ammonium cyanide is a salt derived from ammonium hydroxide and hydrocyanic acid. In water ammonium cyanide hydrolyzes in accordance with the equation,

$$NH_4^+ + CN^- + H_2O = NH_4OH + HCN \tag{9}$$

The equilibrium expression for this reaction is

$$\frac{(NH_4OH)(HCN)}{(NH_4^+)(CN^-)} = K_H$$

By multiplying both the numerator and the denominator by $(H^+)(OH^-)$, it can easily be shown that

$$K_H = \frac{K_W}{K_I \text{ (acid)} \times K_I \text{ (base)}} \tag{10}$$

The salts of polybasic acids hydrolyze in two or more steps. For example, sodium sulfide, Na_2S, a salt of a dibasic acid, hydrolyzes as follows:

$$S^{--} + H_2O = HS^- + OH^- \tag{11}$$

and

$$HS^- + H_2O = H_2S + OH^- \tag{12}$$

The hydrolysis constant for reaction (11) is

$$\frac{(HS^-)(OH^-)}{(S^{--})} = \frac{K_W}{K_2} = \frac{1 \times 10^{-14}}{1.3 \times 10^{-13}} = .077$$

and that for reaction (12) is

$$\frac{(H_2S)(OH^-)}{(HS^-)} = \frac{K_W}{K_1} = \frac{1 \times 10^{-14}}{1 \times 10^{-7}} = 1 \times 10^{-7}$$

It will be observed that the hydrolysis constant for reaction (11) is very much larger than that for reaction (12). This fact is very significant, for it means that the hydrolysis produced by the second step is negligible as compared with that for the first step, and in calculating the hydroxide ion concentration or the sulfide ion concentration in solutions of soluble sulfides only the first step of hydrolysis need be considered.

Note that in equation (11) for the hydrolysis of the sulfide ion (***first*** step) an equilibrium exists between the sulfide ion and the bisulfide ion. The same ions are also involved in the equilibrium for the ***second*** step of ionization of hydrogen sulfide ($HS^- = H^+ + S^{--}$). Therefore in calculating the hydrolysis constant for the ***first*** step of hydrolysis, K_W and the ionization constant for the ***second*** step of ionization are involved. Conversely, the ***second*** step of hydrolysis (equation 12) is concerned with the ***first*** step of ionization of hydrogen sulfide, ($H_2S = H^+ + HS^-$).

The concentration of the hydrogen ion produced in solutions of salts of weak acids and strong bases, besides varying with the concentration of the salt, varies considerably from salt to salt, depending upon the relative weakness of the acid which is formed in the hydrolysis process. The larger the hydrolysis constant for such a salt, the greater will be the degree or extent of hydrolysis, and therefore the greater the hydroxide ion concentration. *The degree of hydrolysis is the fractional amount of the ions which hydrolyze*, i.e., the fractional part of the ions of the weak acid or base that have reacted with water. Equation (5) tells us that the hydrolysis constant will be larger the smaller the dissociation constant for the acid, i.e., the weaker the acid. The hydroxide ion concentration in a 0.1 molar solution of sodium acetate is about 10^{-5} molar; in a solution, 0.1 molar in sodium cyanide, about 10^{-3} molar; in a 0.1 molar solution of sodium carbonate, approximately 5×10^{-3} molar,

while that in a 0.1 molar solution of sodium sulfide is almost .06 molar. In the last case about 60 percent of the sulfide ion hydrolyzes to produce the hydroxide ion. These examples are summarized in Table 24. Note that as the constant for the acid decreases the constant for hydrolysis and the hydroxide ion concentration increases.

TABLE 24

HYDROLYSIS OF SALTS OF WEAK ACIDS

Solution	Weak acid formed	K_I	K_H	(OH^-) in. 0.1 M soln (approx.)
Sodium nitrite	Nitrous	4.6×10^{-4}	2.2×10^{-11}	1.5×10^{-6}
Sodium acetate	Acetic	1.85×10^{-5}	5.4×10^{-10}	7×10^{-6}
Sodium carbonate	Bicarbonate ion	4.8×10^{-11}	2.1×10^{-4}	5×10^{-3}
Sodium sulfide	Bisulfide ion	1.3×10^{-13}	.077	6×10^{-2}

Examples of Hydrolysis. When a solution of ferric chloride is added to one containing sodium carbonate, a dark red precipitate of ferric hydroxide is formed and carbon dioxide is liberated from the solution. The hydroxide ion concentration in the sodium carbonate solution, formed by hydrolysis, is sufficient to precipitate the ferric hydroxide. Even though the carbonate ion concentration in the solution may be more than 100 times as great as the hydroxide ion concentration, the ferric hydroxide will still precipitate in preference to ferric carbonate. If ferric carbonate were very insoluble as compared with ferric hydroxide, this would not be the case. Then the carbonate would precipitate in preference to the hydroxide. (If a soluble silver salt is added to a solution containing sodium carbonate, the carbonate and not the hydroxide (or oxide) will precipitate.)

The reaction taking place when ferric hydroxide is precipitated by a solution of sodium carbonate is

$$Fe^{+++} + 3CO_3^{--} + 3H_2O = 3HCO_3^- + Fe(OH)_{3(s)} \quad (13)$$

This is followed by the reaction,

$$Fe^{+++} + 3HCO_3^- + 3H_2O = 3H_2CO_3 + Fe(OH)_{3(s)} \quad (14)$$

The carbonic acid formed in the last reaction breaks down into water and carbon dioxide. It is to be noted that it is only by virtue of the hydrolysis of the carbonate and bicarbonate ions that the precipitation of ferric hydroxide takes place. These reactions may be written:

$$CO_3^{--} + H_2O = HCO_3^- + OH^- \quad (15)$$

$$HCO_3^- + H_2O = H_2CO_3 + OH^- \quad (16)$$

The ferric ion may then be considered to combine with the hydroxide ion produced by equations (15) and (16) to form ferric hydroxide:

$$Fe^{+++} + 3OH^- = Fe(OH)_{3(s)} \quad (17)$$

However, the over-all reaction includes only those substances which ultimately disappear and those which are formed and is expressed by the summation of equations (13) and (14).

$$2Fe^{+++} + 3CO_3^{--} + 6H_2O = 3H_2CO_3 + 2Fe(OH)_{3(s)} \quad (18)$$

The soluble aluminum and chromium salts behave in an entirely analogous manner; aluminum hydroxide, $Al(OH)_3$, and chromium hydroxide, $Cr(OH)_3$, are formed in these cases. The same argument that has been given for the precipitation of ferric hydroxide by the carbonate solution may be applied, part for part, to the precipitation of the hydroxides of these two metals.

Ferric hydroxide is so insoluble that it may be precipitated from a solution containing a ferric salt by the addition of the relatively insoluble barium carbonate. The small amount of carbonate ion which enters the solution ($K_{S.P.}BaCO_3 = 1.6 \times 10^{-9}$) is sufficient to produce enough hydroxide ion to precipitate ferric hydroxide, but (CO_3^{--}) is not great enough to precipitate the carbonates of the zinc group. Therefore, since the hydroxides of the aluminum group are precipitated by this solution, $BaCO_3$ is sometimes used as a means for the separation of the zinc and the aluminum groups.

Ferrous hydroxide, $Fe(OH)_2$, is not precipitated by solutions of soluble carbonates. The basic ferrous carbonate,

$Fe_2(OH)_2CO_3$, is sufficiently insoluble so that it precipitates in preference to the normal carbonate when a solution of sodium carbonate is added to one containing ferrous ion. If, however, ammonium carbonate is used in place of the sodium carbonate solution, ferrous carbonate rather than the basic ferrous carbonate will be precipitated. The presence of the ammonium ion in the ammonium carbonate solution lowers the hydroxide ion concentration (ammonium hydroxide is formed) to such an extent that the precipitation of ferrous carbonate is favored. As would be expected, the hydroxide ion concentration in a solution of ammonium carbonate, due to the hydrolysis of the ammonium ion, is smaller than the hydroxide ion concentration in a solution of sodium carbonate of the same concentration. The hydrolysis of the ammonium ion furnishes hydrogen ions which in turn use up available hydroxide ions in the solution.

When salts are said to be unstable in solution, these substances usually are decomposed in solution through hydrolysis with the formation of a precipitate or with the evolution of a gas. Aluminum sulfide, for example, when dissolved in water will form the insoluble aluminum hydroxide and hydrogen sulfide gas will be evolved. The aluminum ion, Al^{+++}, first formed reacts with the hydroxide ion of water, and the sulfide ion with the hydrogen ion of water. The net result of this double hydrolysis is

$$2Al^{+++} + 3S^{--} + 6H_2O = 2Al(OH)_{3(s)} + 3H_2S_{(g)} \qquad (19)$$

There are many examples of salts of this kind that cannot be dissolved in water and recovered again by crystallization. In fact, many salts hydrolyze to such an extent that they are decomposed by the water vapor in air.

When a relatively insoluble carbonate such as barium carbonate, $BaCO_3$, is dissolved in water an appreciable amount of the carbonate ion hydrolyzes to form the bicarbonate ion. The concentration of the barium ion accordingly is not the same as the concentration of the carbonate ion under these conditions. The concentration of the barium ion is practically

equal to the sum of the concentrations of the carbonate and bicarbonate ions. Through this process of hydrolysis the solution becomes very slightly alkaline. This equilibrium is represented in the following equation:

$$\begin{aligned} BaCO_3(\text{solid}) &= Ba^{++} + CO_3^{--} \\ &\quad + \\ &\quad H_2O = HCO_3^- + OH^- \end{aligned}$$

or, $$BaCO_3(\text{solid}) + H_2O = Ba^{++} + HCO_3^- + OH^- \qquad (20)$$

The hydrolysis of the bicarbonate ion to form carbonic acid and hydroxide ion is negligible.

The relatively insoluble sulfides behave in exactly the same way; the sulfide ion hydrolyzes to give bisulfide and hydroxide ions. In calculating the solubility of either a relatively insoluble sulfide or carbonate from the solubility product constant, account must be taken of this hydrolysis process which involves the sulfide or the carbonate ion, as the case may be.

The concentrations of the different ions in equilibrium in a solution of a soluble bicarbonate such as sodium bicarbonate, $NaHCO_3$, cannot be accounted for by a simple process of hydrolysis. The equilibrium in this case is somewhat more complicated. The bicarbonate ion hydrolyzes to produce carbonic acid and the hydroxide ion,

$$HCO_3^- + H_2O = H_2CO_3 + OH^- \qquad (21)$$

but the bicarbonate ion produces hydrogen ion through dissociation.

$$HCO_3^- = H^+ + CO_3^{--} \qquad (22)$$

The hydrogen ion and the hydroxide ion produced according to equations (22) and (21) respectively, will combine to form water. If processes (21) and (22) were to occur to the same extent, then a solution of sodium bicarbonate would be neutral. By experiment we find that a sodium bicarbonate solution is very slightly alkaline, a fact which indicates that process (21) occurs to a slightly greater extent than process (22). By

summing up the reactions considered above, we obtain the over-all reaction,

$$2HCO_3^- = H_2CO_3 + CO_3^{--} \qquad (23)$$

The H_2CO_3 and the CO_3^{--} ion concentrations in a solution of sodium bicarbonate are very nearly the same.

Hydrolysis must also be taken into account to explain the properties of some of the common substances that are encountered in everyday life. Lye (sodium hydroxide) and ammonium hydroxide are two well known cleansing agents. The cleansing property of these substances is attributed in part to the hydroxide ion which reacts with fats and oils to produce soaps. Since the hydroxide ions can be produced by the hydrolysis of salts of weak acids, these substances also have the same property as that of the two hydroxides just mentioned. The common salts used for this purpose are washing soda, Na_2CO_3, borax, $Na_2B_4O_7$, water glass, Na_2SiO_3, and tri-sodium phosphate, Na_3PO_4. The weaker the acid which is produced by hydrolysis, the greater will be the concentration of the hydroxide ions. Of the four substances just considered, tri-sodium phosphate produces the greatest hydroxide ion concentration, since the ion, HPO_4^{--}, is the weakest acid involved.

$$PO_4^{---} + H_2O = HPO_4^{--} + OH^- \qquad (24)$$

Sodium silicate is one of the constituents of laundry soap and through its hydrolysis action increases the concentration of the hydroxide ion of the soap solution. Washing powders contain some hydrolyzable salt.

The common constituent of all baking powders is sodium bicarbonate. The other chief constituent is a substance which in solution furnishes the hydrogen ion which reacts with the bicarbonate ion to produce carbon dioxide gas. In some brands of baking powders the hydrogen ion is produced by a weak acid such as tartaric acid or an acid salt, while in others aluminum sulfate is used, which through the process of hydrolysis produces the hydrogen ion and aluminum hydroxide.

The Neutralization of Weak Acids and Weak Bases. When 0.1 mole of hydrochloric acid is neutralized in solution by 0.1 mole of sodium hydroxide, the solution produced could be exactly reproduced by the addition of 0.1 mole of sodium chloride to the same amount of water. When the acid and the base have just neutralized each other, the solution is neither acidic nor alkaline, for sodium chloride does not hydrolyze. If, on the other hand, 0.1 mole of acetic acid is neutralized in solution by exactly 0.1 mole of sodium hydroxide, the sodium acetate solution does not contain the same number of hydrogen ions as hydroxide ions. When a weak acid is neutralized by a strong base the end point of the neutralization does not occur when the concentrations of the hydrogen and hydroxide ions are the same, but rather when the solution is slightly alkaline. The concentration of the hydrogen ion or of the hydroxide ion at the neutralization point will depend upon the concentrations of the substances involved and upon the ionization constant of the acid formed in the hydrolysis process.

The process of neutralization of weak acids by strong bases may be illustrated by a specific example. Suppose 50 ml. of a 0.1 molar solution of hydrocyanic acid, HCN, is to be neutralized by 50 ml. of a 0.1 molar solution of sodium hydroxide. What will be the hydrogen and hydroxide ion concentrations at the point of neutralization? The final solution, through the addition of the two equal volumes, will be .05 molar with respect to sodium cyanide. The problem is then to calculate the hydrogen ion and the hydroxide ion concentrations in this solution. The equation representing the hydrolysis equilibrium is

$$CN^- + H_2O = HCN + OH^- \qquad (25)$$

Let X be the concentration of the hydroxide ion. Then X must also be the concentration of the HCN, and $.05 - X$ is the concentration of the cyanide ion at equilibrium. Since we might expect the amount of cyanide ion hydrolyzed to be small as compared with the total amount of cyanide ion present, we may simplify this and let the concentration of the cyanide

ion be practically equal to .05 molar rather than $.05 - X$. Then,

$$\frac{(HCN)(OH^-)}{(CN^-)} = \frac{X^2}{.05} = \frac{K_W}{K_A} = \frac{10^{-14}}{4 \times 10^{-10}} = 2.5 \times 10^{-5}$$

$$X^2 = 1.25 \times 10^{-6}$$

$$X = 1.1 \times 10^{-3} \text{ mole per liter} = (OH^-)$$

The concentration of the hydrogen ion is $\frac{10^{-14}}{1.1 \times 10^{-3}} = 9 \times 10^{-12}$ mole per liter. The hydrogen ion concentration in this solution is 11,000 times smaller than that for pure water (10^{-7} molar), and the hydroxide ion concentration is 11,000 times larger.

In selecting an indicator for this reaction under the conditions stipulated above, we should choose one that changes color as near as possible to the calculated hydrogen ion concentration. By referring to the table on page 137, we find that thymol phthalein would be the most suitable indicator. If methyl orange were used, the final solution obtained would still contain a large excess of the acid at the end point and would not be neutralized.

Buffer Solutions. Buffer solutions are solutions containing weak acids or weak bases together with the salts of weak acids or bases and have the property of maintaining a hydrogen ion concentration which is affected only slightly by the addition of appreciable amounts of either acid or base.

A solution containing 0.1 mole of acetic acid and 0.1 mole of sodium acetate per liter is such a buffer solution. Its hydrogen ion concentration is about 1.85×10^{-5} molar. A solution containing 1.85×10^{-5} mole of hydrochloric acid per liter would also have the same hydrogen ion concentration as the buffer solution described above, but its action toward acids and bases would be entirely different from that of the buffer solution. If 1.85×10^{-5} mole of sodium hydroxide is added to 1 liter of the above hydrochloric acid solution, the resulting solution would be neutral to the hydrogen ion, i.e., the hydrogen ion concentration would be 10^{-7} molar. Upon the addition

of 1.85×10^{-5} mole of sodium hydroxide to 1 liter of the buffer solution, the hydrogen ion concentration would not be appreciably affected.

To understand better the action of the buffer solution, let us consider the equilibrium between the acid and its ions:

$$HAc = H^+ + Ac^-$$

$$\frac{(H^+)(Ac^-)}{(HAc)} = 1.85 \times 10^{-5}$$

$$(H^+) = \frac{(HAc)}{(Ac^-)} \times 1.85 \times 10^{-5} \qquad (26)$$

When the concentrations of the acetic acid molecules and of the acetate ions are made equal as they were in the example above, the concentration of the hydrogen ion has the same value as the dissociation constant. If as much as .05 mole of sodium hydroxide is added to 1 liter of the buffer solution (0.1 mole acetic acid and 0.1 mole of sodium acetate per liter), the hydrogen ion concentration will be affected relatively little. Under these conditions, .05 mole of the acetic acid has been neutralized by the added sodium hydroxide, and the solution now consists of .05 mole acetic acid and 0.15 mole of sodium acetate. Now the hydrogen ion concentration is

$$(H^+) = \frac{(HAc)}{(Ac^-)} \times 1.85 \times 10^{-5} = \frac{.05}{0.15} \times 1.85 \times 10^{-5} = 0.6 \times 10^{-5}$$

The hydrogen ion concentration has been lowered only threefold by the addition of the sodium hydroxide. In a like manner, the addition of .05 mole of hydrochloric acid to the original buffer solution will increase the hydrogen ion concentration only threefold. In this case, the hydrogen ions produced by the hydrochloric acid combine with the acetate ions and are removed in the form of acetic acid molecules. After the hydrochloric acid has been added, the final solution will contain 0.15 mole of acetic acid and .05 mole of acetate ion and

$$(H^+) = \frac{0.15}{.05} \times 1.85 \times 10^{-5} = 5.5 \times 10^{-5} \text{ mole per liter}$$

The following table illustrates the buffer action of an acetic acid–sodium acetate solution in its ability to absorb either a strong acid, such as hydrochloric acid, or a strong base, such as sodium hydroxide, with but little change in the concentration of the hydrogen ion. By adding as much as

TABLE 25

BUFFER ACTION OF A SOLUTION CONTAINING 0.1 MOLE OF ACETIC ACID AND 0.1 MOLE OF SODIUM ACETATE PER LITER

ml. of 0.1 molar NaOH added to 1 liter of buffer solution	(H^+) of final solution	ml. of 0.1 molar HCl added to 1 liter of buffer solution	(H^+) of final solution
0	0.0000185	0	0.0000185
5	0.0000183	5	0.0000187
10	0.0000181	10	0.0000189
25	0.0000175	25	0.0000195
50	0.0000167	50	0.0000204
75	0.0000159	75	0.0000215
100	0.0000151	100	0.0000226

100 ml. of either 0.1 molar hydrochloric acid solution or 0.1 molar sodium hydroxide solution to 1 liter of the buffer solution, the hydrogen ion concentration remains within the limits 1.51×10^{-5} and 2.26×10^{-5} mole per liter. By this treatment the hydrogen ion concentration of the original solution does not vary more than 25 percent. In contrast to this, if 100 ml. of 0.1 molar hydrochloric acid were added to pure water, the hydrogen ion concentration would increase 100,000-fold.

The above solution was such as to maintain the hydrogen ion concentration in the neighborhood of 10^{-5} molar. If it is desired to maintain the hydrogen ion concentration at a different value, a different acid and salt should be chosen. If it is desired to maintain the hydrogen ion concentration at about 10^{-9} molar (OH^- ion concentration of 10^{-5} molar), then hydro-

cyanic acid and potassium cyanide might be used, for this acid has an ionization constant equal to 4×10^{-10}. However, for most work this acid would be unsuitable because of its toxic nature.

Ions and salts of polybasic acids also form buffer solutions. For example, a solution of sodium bicarbonate is a buffer solution. The bicarbonate ion, HCO_3^-, is an ion of a salt of a weak acid; $NaHCO_3$ is the salt and H_2CO_3 the acid from which it is derived. Furthermore, the bicarbonate ion is itself a weak acid, dissociating to form hydrogen ions and carbonate ions. When hydrochloric acid is added to a solution of sodium bicarbonate, carbonic acid is formed and the hydrogen ion concentration of the solution is changed very little. If sodium hydroxide is added to this same solution, the carbonate ion is formed,

$$HCO_3^- + OH^- = H_2O + CO_3^{--} \qquad (27)$$

and again the hydrogen ion concentration is little affected.

Blood is a good example of a buffer solution. The principal ion and acid responsible for the buffer action of blood are the HCO_3^- ion and H_2CO_3. When excess hydrogen ion enters the blood stream it is absorbed principally by the reaction

$$H^+ + HCO_3^- = H_2CO_3 \qquad (28)$$

and when excess hydroxide ion is formed it disappears through the reaction

$$OH^- + H_2CO_3 = H_2O + HCO_3^- \qquad (29)$$

By this mechanism the hydrogen ion concentration in the blood stream remains remarkably constant — very slightly alkaline. Besides the HCO_3^- and H_2CO_3, there are other buffering substances, such as HPO_4^{--}, $H_2PO_4^-$, and hemoglobin, which also help control the H^+ ion concentration.

When carbon dioxide is produced in the tissues by metabolic processes, carbonic acid is formed, which in turn dissociates to produce hydrogen and bicarbonate ions. The hydrogen ion produced by this reaction is absorbed by the buffer action of the blood. When oxygen is breathed into the

lungs it reacts with the hemoglobin and as a result of this reaction the hemoglobin becomes a stronger acid and a large excess of hydrogen ions results. These hydrogen ions, which locally cannot be completely absorbed by the buffer action of the blood, now combine with the bicarbonate ions to form excess carbonic acid (CO_2 and H_2O). The carbon dioxide is then exhaled from the lungs.

The Hydrolysis of Metal Ions. A large number of metal ions hydrolyze to give acid solutions. We therefore conclude that the corresponding bases of these ions are weak. Many of these metal ions form polyacid bases, i.e., more than one ionizable OH radical is associated with the metal ion. Before considering the problem of the hydrolysis of these ions let us first examine the properties of these polyacid bases. Most of the polyacid bases are very insoluble, e.g., $Al(OH)_3$, $Pb(OH)_2$ and $Fe(OH)_3$. Without doubt these hydroxides ionize in two or more stages just as polybasic acids ionize in more than one stage. The equilibrium reactions between $Fe(OH)_3$, for example, and its ions, when it is dissolved in water, can be expressed by the following equations.

$$Fe(OH)_{3(s)} = Fe(OH)_{3(soln)} \tag{30}$$

$$Fe(OH)_{3(soln.)} = Fe(OH)_2^+ + OH^- \tag{31}$$

$$Fe(OH)_2^+ = Fe(OH)^{++} + OH^- \tag{32}$$

$$Fe(OH)^{++} = Fe^{+++} + OH^- \tag{33}$$

Just as there are no polybasic acids which in moderate concentration ionize to the extent of 100 per cent in any but the first stage of ionization so we may assume that polyacid bases behave similarly. But it must be borne in mind that most of the polyacid bases are very insoluble and therefore the concentrations of the ions in equilibrium with them must be very small. Because of the small concentration — which is equivalent to a very high dilution in solutions of soluble bases — all stages can be considered as being practically completely dissociated.

Zinc hydroxide, for example, is very insoluble. Therefore

the amount of undissociated and dissolved $Zn(OH)_2$ in equilibrium with the solid must be very small.

$$Zn(OH)_{2(s)} = Zn(OH)_{2(soln.)} \tag{34}$$

The undissociated $Zn(OH)_2$ will ionize first as

$$Zn(OH)_{2(soln.)} = Zn(OH)^+ + OH^- \tag{35}$$

and then will be further ionized in the following manner:

$$Zn(OH)^+ = Zn^{++} + OH^- \tag{36}$$

Just as a 1×10^{-5} *M* solution of HAc is ionized to the extent of 70 percent, while a 1 *M* solution is ionized to the extent of only 0.4 percent so, because of the low concentration, we might expect these insoluble bases to be highly ionized in spite of the fact that the ionization constants may be small. We lack data on the ionization constants for the various steps involved in the dissociation of most polyacid bases and therefore we group all stages of dissociation into a single reaction. For example, reactions (34), (35), and (36) may be grouped into the one reaction

$$Zn(OH)_{2(s)} = Zn^{++} + 2OH^- \tag{37}$$

In view of the extreme insolubility of many polyacid bases this procedure will often be satisfactory. But when we consider the hydrolysis of the metal ions the problem is quite different since the concentration of these ions is usually not small.

If 0.1 mole of $ZnCl_2$ is dissolved in one liter of water the solution is found to be decidedly acidic. The reason for this is that the Zn^{++} ion undergoes hydrolysis, the first stage of which may be represented by the equation

$$Zn^{++} + H_2O = Zn(OH)^+ + H^+ \tag{38}$$

The concentration of the Zn^{++} ion is high (approximately 0.1 *M*) but since the amount of hydrolysis is relatively small the concentrations of the $Zn(OH)^+$ and of the H^+ ions are small. The second stage of hydrolysis is much smaller than that of the first stage and may be neglected, since the concen-

tration of the $Zn(OH)^+$ ion is itself very small. However, the reaction for the second stage of hydrolysis is

$$Zn(OH)^+ + H_2O = Zn(OH)_{2(soln.)} + H^+ \qquad (39)$$

To calculate the hydrolysis constant for equation (38) it is necessary that we know the value of the ionization constant for equation (36). It cannot be calculated by using the ionization constant for equation (37). The ionization constant for (36) is known to have a value of 4×10^{-5}. The hydrolysis constant for the reaction represented by equation (38) is therefore equal to

$$\frac{(Zn(OH)^+)(H^+)}{(Zn^{++})} = \frac{K_W}{K_{2(base)}} = \frac{1 \times 10^{-14}}{4 \times 10^{-5}} = 2.5 \times 10^{-10} = K_H$$

If we let X equal the number of moles of Zn^{++} ion undergoing hydrolysis, then at equilibrium $(Zn(OH)^+)$ will be X, (H^+) will also equal X, and (Zn^{++}) will have a value of $(0.1 - X)$. Neglecting X as compared with 0.1 we have

$$\frac{X^2}{0.1} = 2.5 \times 10^{-10} \quad \text{or} \quad X^2 = 25 \times 10^{-12}$$

$$X = 5 \times 10^{-6} \text{ mole per liter} = (H^+)$$

Therefore the degree of hydrolysis is $\frac{5 \times 10^{-6}}{0.1}$ or 5×10^{-5}.

On a percentage basis the extent of hydrolysis is therefore .005 percent. The solution is found to be decidedly acidic, according to the calculation we have just carried out.

The constants for the different stages of ionization are not known for most hydroxides. Therefore we cannot calculate the hydrolysis constants for most positive metal ions which we know are hydrolyzed in solution.

If the hydroxide of a metal ion is insoluble we may conclude that the metal ion will hydrolyze to give an acidic solution. We base this conclusion on the assumption that the insolubility of the hydroxide is in part due to a firm binding between the metal ion and the OH^- ions. We may also assume that if all

of the OH^- ions are held firmly, for example by the Al^{+++} ion in forming $Al(OH)_3$, then there should also be a firmer binding between the Al^{+++} ion and the first OH^- ion to form $Al(OH)^{++}$. If such is the case, Al^{+++} ion in water should hydrolyze. This reasoning can be applied to any ion which forms an insoluble hydroxide; the facts are in accord with this postulate. Practically all metal ions other than those of the alkali or alkaline earth groups hydrolyze to give acidic solutions.

It has been our custom to write the symbol for a multivalent positive ion in its simplest form. For example, if $SnCl_4$ is dissolved in water we often write the formula for the resulting stannic ion as Sn^{++++}. Certainly this cannot be correct. Very probably most of the ions in such a solution are present as $SnCl^{+++}$ and $SnCl_2^{++}$ ions and very few of them are in the form of Sn^{++++} ion. If HCl is present in the solution in excess, then the predominating ion is probably $SnCl_6^{--}$. However, we have no definite information relative to the composition of many ions of this type and therefore we use the simplest symbols or formulae possible. The same situation undoubtedly exists with Fe^{+++}, Al^{+++} and other trivalent and higher valent ion salts.

Hydrolysis and the Brønsted Definitions.* If the Brønsted definitions of acids and bases are to be adopted consistently, then the term hydrolysis becomes superfluous. What the older established definitions called hydrolysis becomes merely an acid-base reaction. But the terms hydrolysis and salt have become so firmly entrenched in chemical thought and in chemical literature that hydrolysis cannot be brushed aside without consideration. The introduction of this term into the Brønsted definitions, however, is apt to lead to some confusion if hydrolysis is not already understood in the light of the older definitions.

According to the older established definitions ions which hydrolyze in water solution can be divided into two classes; those which produce acidic and those which produce basic

* Before reading this section the student is advised to review the section on the Brønsted Definitions of Acids and Bases on pages 139–147.

solutions. Let us consider these two types of hydrolysis separately and as an example of the first kind let us consider the hydrolysis of the ammonium ion. According to the older definitions the equation for the hydrolysis reaction is

$$NH_4^+ + H_2O = NH_4OH + H^+ \qquad (40)$$

The mental picture for the process is that of competition between the H^+ ion and the NH_4^+ ion for the OH^- ion. As the result of this competition, some H^+ ions are left in excess of OH^- ions and the solution is acidic.

According to the Brønsted definitions this same hydrolysis reaction is expressed as follows.

$$\underset{\text{Acid}_1}{NH_4^+} + \underset{\text{Base}_2}{H_2O} = \underset{\text{Base}_1}{NH_3} + \underset{\text{Acid}_2}{H_3O^+} \qquad (41)$$

Examining equations (40) and (41) formally we see that the difference between them is that in equation (40) the water molecule is associated with the NH_3 molecule to form NH_4OH (a formula which emphasizes the basic nature of ammonia in water solution), and in equation (41) the water is associated with the H^+ ion, which is written as H_3O^+. According to the Brønsted definitions equation (41) represents merely an acid-base reaction and the NH_4^+ ion is regarded as a weak acid. The NH_3 and the H_2O molecules are competing for the proton. Equation (40) does not represent the actual process taking place any more than does equation (41); these details of the reaction are not known. Whether one uses equation (41) or equation (40), i.e., Brønsted or the older established definitions, is merely a question of convenience and ease of acquiring an understanding of the acid-base reaction in solution.

According to the older definitions hydrolysis is the reverse of neutralization, i.e., equation (40) reading from right to left represents a process of neutralization while from left to right, it represents hydrolysis. With the Brønsted definitions the reactions represented by both directions of equation (41) are acid-base reactions. Only if we borrow the concepts of hydrolysis and of neutralization from the older definitions may we define the process from left to right in equation (41) as

hydrolysis and the process from right to left as neutralization. In general, on the basis of the newer definitions, hydrolysis is defined as a proton transfer reaction between a cation-acid or an anion-base and water, to produce the hydronium ion or the hydroxide ion respectively. But again it must be emphasized that if the Brønsted definitions had been common usage for many years the term hydrolysis in inorganic chemistry would not be necessary.

Let us consider the equilibrium expression for reaction (41) and show the relationship between the constant for this expression and the constants for other reactions from which the value of the former may be calculated. As has been previously pointed out, reaction (41) may be regarded as one of dissociation of a weak acid, and its constant may then be designated as $K^{B}_{I\,(acid)}$.*

$$K^{B}_{I\,(acid)} = \frac{(NH_3)(H_3O^+)}{(NH_4^+)} \tag{42}$$

The concentration of the water molecules is omitted from the expression since its value remains constant for all practical purposes. Consider next the two reactions

$$H_2O + H_2O = H_3O^+ + OH^- \tag{43}$$

and

$$NH_3 + H_2O = NH_4^+ + OH^- \tag{44}$$

The equilibrium expressions for (43), (44) are $(H_3O^+)(OH^-)$ and $\frac{(NH_4^+)(OH^-)}{(NH_3)}$ respectively. The first of these is equal to the equilibrium constant for water and is denoted by K_W^B, the second we shall denote merely by K_{eq}^{B}.

$$K_W^B = (H_3O^+)(OH^-) \tag{45}$$

$$K_{eq}^{B} = \frac{(NH_4^+)(OH^-)}{(NH_3)} \tag{46}$$

* Constants referring to the Brønsted definitions are distinguished from those of the older definitions by the superscript B.

From equation (45) $(H_3O^+) = \dfrac{K_W{}^B}{(OH^-)}$

Substituting $\dfrac{K_W{}^B}{(OH^-)}$ for (H_3O^+) in equation (42), we obtain

$$K^B_{I(acid)} = \frac{(NH_3)K_W{}^B}{(NH_4^+)(OH^-)} = \frac{K_W{}^B}{\dfrac{(NH_4^+)(OH^-)}{(NH_3)}} \tag{47}$$

But the denominator in the last expression in equation (47) is equal to $K_{eq}{}^B$ (equation 46). Therefore

$$K^B_{I(acid)} = \frac{K_W{}^B}{K_{eq}{}^B} \tag{48}$$

Let us now return to the older definitions with which we previously showed that

$$K_H = \frac{K_W}{K_{I(base)}} \tag{49}$$

What was previously called the hydrolysis constant is now the acid constant ($K^B_{I(acid)}$ is equivalent to K_H), and what was previously known as the dissociation constant for the base is designated merely as an equilibrium constant, ($K_{eq}{}^B$ is equivalent to $K_{I(base)}$). Obviously $K_W{}^B$ is the same as K_W. Again we see only different names for the same phenomena; the relationships are the same.

Let us next consider the hydrolysis of an anion to produce an alkaline solution, and as an example we shall again use the acetate ion.

$$\underset{\text{Acid}_1}{H_2O} + \underset{\text{Base}_2}{Ac^-} = \underset{\text{Acid}_2}{HAc} + \underset{\text{Base}_1}{OH^-} \tag{50}$$

The hydrolysis reaction is expressed by the same equation (50) whether the Brønsted or the older definitions are used; the terminology only is different. The equilibrium expression for the reaction is $\dfrac{(HAc)(OH^-)}{(Ac^-)}$.

By the older terminology this expression is equal to the hydrolysis constant. By the Brønsted definitions it would more properly be called an acid-base equilibrium constant. Thus,

$$\frac{(\mathrm{HAc})(\mathrm{OH^-})}{(\mathrm{Ac^-})} = K_{\mathrm{eq}}{}^{\mathrm{B}} \tag{51}$$

It can be shown that

$$K_{\mathrm{eq}}{}^{\mathrm{B}} = \frac{K_{\mathrm{W}}{}^{\mathrm{B}}}{K^{\mathrm{B}}_{\mathrm{I(acid)}}} \tag{52}$$

where $K^{\mathrm{B}}_{\mathrm{I(acid)}}$ is the constant for the reaction

$$\mathrm{HAc} + \mathrm{H_2O} = \mathrm{H_3O^+} + \mathrm{Ac^-} \tag{53}$$

Using the older definitions, we previously showed that

$$K_{\mathrm{H}} = \frac{K_{\mathrm{W}}}{K_{\mathrm{I(acid)}}} \tag{54}$$

In this case the older K_{H} is equivalent to the newer $K_{\mathrm{eq}}{}^{\mathrm{B}}$.

The $\mathrm{Ac^-}$ ion is known as a strong base; it has a great tendency to take up protons. The strongly basic character of the $\mathrm{Ac^-}$ ion may be visualized in terms of the older concepts if we consider it in its hydrated form. Suppose that instead of representing the acetate ion by the symbol $\mathrm{Ac^-}$ we used $\mathrm{AcHOH^-}$ $(\mathrm{Ac^-} + \mathrm{H_2O})$; i.e., included in its formula one molecule of water. Then it is easy to see that if the $\mathrm{OH^-}$ ion dissociated from this complex the HAc molecule would be formed and the stronger the base, the greater the concentration of $\mathrm{OH^-}$ ions produced. The tendency to acquire protons is equivalent to a tendency to produce $\mathrm{OH^-}$ ions.

$$\mathrm{AcHOH^-} = \mathrm{HAc} + \mathrm{OH^-} \tag{55}$$

This reaction is effectively the same as that represented by equation (50). This procedure, however, is not conventional. The hydrolysis of positive metal ions, according to the Brønsted definitions, will be considered in the next chapter.

Examples of Hydrolysis Problems

Example 1.

(a) Calculate the concentration of the $\mathrm{OH^-}$ ion in a 0.1 *M* NaAc solution.

(b) What is the value of the concentration of the $\mathrm{H^+}$ ion in this same solution?

(c) What is the degree of hydrolysis?

Sodium acetate is the salt of a strong base and a weak acid and therefore its solution will show an alkaline reaction. The equation representing the hydrolysis reaction is

$$\underset{\text{Concentrations:}}{} \quad \begin{matrix} Ac^- + H_2O = HAc + OH^- \\ (0.1 - X) \qquad X \qquad X \end{matrix}$$

Therefore

$$\frac{(HAc)(OH^-)}{(Ac^-)} = \frac{X^2}{0.1 - X} = \frac{K_W}{K_I} = \frac{1 \times 10^{-14}}{1.85 \times 10^{-5}} = 0.54 \times 10^{-9}$$

Neglecting X as compared with 0.1 in the denominator of the second expression, we have

$$\frac{X^2}{0.1} = 0.54 \times 10^{-9}$$

$$X^2 = 0.54 \times 10^{-10}$$

$$X = 0.75 \times 10^{-5} \text{ mole per liter} = (OH^-) = (HAc)$$

To calculate (H^+) we use the dissociation constant for water.

$$(H^+) = \frac{K_W}{(OH^-)} = \frac{1 \times 10^{-14}}{0.75 \times 10^{-5}} = 1.3 \times 10^{-9} \text{ mole per liter}$$

It is also possible to calculate the (H^+) in the following way. The HAc in solution is in equilibrium with its two ions, H^+ and Ac^-. The concentration of the undissociated HAc in this solution is the same as that of the OH^- ion and was found to be 0.75×10^{-5} M. The value for (Ac^-) is practically 0.1. We may therefore use the ionization constant for HAc to determine the (H^+).

$$\frac{(H^+)(Ac^-)}{(HAc)} = \frac{(H^+) \times 0.1}{0.75 \times 10^{-5}} = 1.85 \times 10^{-5}$$

$$(H^+) = \frac{1.85 \times 10^{-5} \times 0.75 \times 10^{-5}}{0.1}$$

$$(H^+) = 1.3 \times 10^{-9} \text{ mole per liter}$$

The following short-cut method may be used to obtain (H^+) in a solution which hydrolyzes to produce a basic solution:

$$\frac{(HAc)(OH-)}{(Ac^-)} = \frac{X^2}{0.1 - X} = \frac{K_W}{K_I}$$

For generalization let $(Ac^-) = C$; C being the final concentration of the hydrolyzing ion — in this case $.01 - X$, or for practical purposes 0.1, (X is neglected as compared with 0.1). Therefore

$$\frac{(HAc)(OH^-)}{C} = \frac{K_W}{K_I}$$

Since

$$(HAc) = (OH^-)$$

$$(OH^-)^2 = \frac{K_W \times C}{K_I}$$

$$(H^+)^2 = \frac{(K_W)^2}{(OH^-)^2}$$

Therefore

$$(H^+)^2 = \frac{K_W^2 \times K_I}{K_W \times C} = \frac{K_W \times K_I}{C}$$

$$(H^+) = \sqrt{\frac{K_W \times K_I}{C}}$$

Calculating the (H^+) from this last equation we obtain

$$(H^+) = \sqrt{\frac{10^{-14} \times 1.85 \times 10^{-5}}{.1}}$$

$$(H^+) = \sqrt{1.85 \times 10^{-18}}$$

$$(H^+) = 1.3 \times 10^{-9} \text{ mole per liter}$$

The degree of hydrolysis is the fractional amount of the Ac^- ion hydrolyzed. The amount of Ac^- ion which hydrolyzed was X or 0.75×10^{-5} M. Therefore the degree of hydrolysis is X divided by the total amount of Ac^- ion.

$$\text{Degree of hydrolysis} = \frac{X}{0.1} = \frac{0.75 \times 10^{-5}}{0.1} = 7.5 \times 10^{-5}$$

The percent hydrolysis is equal to the degree of hydrolysis multiplied by 100.

$$\text{Percent hydrolysis} = 7.5 \times 10^{-5} \times 100 = .0075 \text{ percent}$$

Example 2.

To 250 ml. of a 0.4 M HCN solution is added 250 ml. of a 0.4 M NaOH solution to give 500 ml. of the mixture. What will be the

value of the (H^+) when the acid and base exactly neutralize each other? $K_I(HCN) = 4 \times 10^{-10}$

Due to the fact that both the HCN and the NaOH solutions have been diluted to 500 ml., the resulting solution would contain these two substances each at a concentration of 0.2 M assuming no reaction to take place. After the reaction takes place and when equilibrium is reached a solution is obtained which would be the same as that produced by adding 0.2 mole of NaCN to a liter of water, or 0.1 mole NaCN to 500 ml. of water. Therefore, the concentration of the CN^- ion in this solution is approximately 0.2 M, but it will be slightly less than this value due to the hydrolysis, as the following equation indicates.

$$CN^- + H_2O = HCN + OH^-$$

Concentrations: $(0.2 - X)$ X X

Then

$$\frac{(HCN)(OH^-)}{(CN^-)} = \frac{X^2}{0.2 - X} = \frac{K_W}{K_{I(acid)}} = \frac{1 \times 10^{-14}}{4 \times 10^{-10}} = 2.5 \times 10^{-5}$$

Neglecting X in comparison with 0.2

$$\frac{X^2}{0.2 - X} \cong \frac{X^2}{0.2} = 2.5 \times 10^{-5}$$

$$X^2 = 5 \times 10^{-6}$$

$$X = 2.2 \times 10^{-3} \text{ mole per liter} = (OH^-)$$

Since

$$(H^+)(OH^-) = 1 \times 10^{-14}$$

$$(H^+) = \frac{1 \times 10^{-14}}{(OH^-)} = \frac{1 \times 10^{-14}}{2.2 \times 10^{-3}}$$

$$(H^+) = 4.5 \times 10^{-12} \text{ mole per liter}$$

Example 3.

(a) Calculate the concentration of the S^{--} ion in a 0.1 M Na_2S solution.

(b) Calculate the degree of hydrolysis of the S^{--} ion.

The hydrolysis of the HS^- ion (second step) is negligible as compared with the hydrolysis of the S^{--} ion (first step).

The reaction is

$$S^{--} + H_2O = HS^- + OH^-$$

Let X be the number of moles of S^{--} ion undergoing hydrolysis. Then, at equilibrium, $(HS^-) = X$, $(OH^-) = X$, and $(S^{--}) = (0.1 - X)$. We then have

$$\frac{(HS^-)(OH^-)}{(S^{--})} = \frac{X^2}{0.1 - X} = K_H = \frac{K_W}{K_{I_2}} = \frac{1 \times 10^{-14}}{1.3 \times 10^{-13}} = 7.7 \times 10^{-2}$$

Since the value of K_H is large, X will be large as compared with 0.1 and we cannot neglect X in the expression $(0.1 - X)$. Accordingly, we must solve this equation by the use of the quadratic solution. Clearing of fractions, we have

$$X^2 = 7.7 \times 10^{-3} - 7.7 \times 10^{-2}X$$

Transposing,

$$X^2 + 7.7 \times 10^{-2}X - 7.7 \times 10^{-3} = 0$$

$$X = .058 \text{ mole per liter} = (HS^-) = (OH^-)$$

$$(0.1 - X) = (S^{--}) = .042 \text{ mole per liter}$$

(See Appendix for the solution of the quadratic equation.)

The degree of hydrolysis is the amount of S^{--} ion hydrolyzed divided by the total amount of S^{--} ion originally present. Therefore

$$\text{Degree of hydrolysis} = \frac{.058}{0.1} = 0.58$$

The percent hydrolysis is 0.58×100 or 58 percent.

Example 4.

What is the *p*H of a solution which contains 0.535 g. of NH_4Cl in 250 ml. of solution?

0.535 g. NH_4Cl is equal to $\frac{0.535}{53.5}$ or .01 mole. .01 mole of NH_4Cl in 250 ml. of solution is equivalent to .04 mole of NH_4Cl per liter. Thus, the concentration of the NH_4^+ ion is .04 M. The NH_4^+ ion undergoes hydrolysis to produce the H^+ ion according to the following equation.

$$NH_4^+ + H_2O = NH_4OH + H^+$$

Let X be the number of moles of NH_4^+ ion undergoing hydrolysis; then, at equilibrium, $(NH_4^+) = (.04 - X)$, $(NH_4OH) = X$, and $(H^+) = X$. Then we have

$$\frac{(NH_4OH)(H^+)}{(NH_4^+)} = \frac{X^2}{.04 - X} = K_H = \frac{K_W}{K_{I(base)}} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

and $$\frac{X^2}{.04 - X} = 5.6 \times 10^{-10}$$

Neglecting X as compared with .04 we have

$$\frac{X^2}{.04} = 5.6 \times 10^{-10}$$

$$X^2 = 22.4 \times 10^{-12}$$

$$X = 4.7 \times 10^{-6} \text{ mole per liter} = (H^+) = (NH_4OH)$$

$$pH = \log \frac{1}{(H^+)} = -\log (H^+)$$

$$\log (H^+) = \log (4.7 \times 10^{-6}) = \log 4.7 + \log 10^{-6}$$
$$= 0.67 + (-6) = -5.33$$

Therefore

$$pH = -\log (H^+) = -(-5.33) = 5.33$$

Example 5.

How many grams of NaAc must be added to 500 ml. of water to give a solution having a pH of 8.52? (Neglect the volume change due to the addition of the salt.)

The reaction is

$$Ac^- + H_2O = HAc + OH^-$$

From the value given for the pH of the solution, the (H^+) may be calculated. Then (OH^-) may be obtained from $K_W = (H^+)(OH^-) = 1 \times 10^{-14}$. In the NaAc solution (HAc) = (OH^-). Having this information, the (Ac^-) in equilibrium with HAc and OH^- ion may be determined from the hydrolysis equilibrium.

$$pH = -\log (H^+) = 8.52$$

$$\log (H^+) = -8.52 = -9.00 + 0.48$$

$$\text{antilog } (-9) = 10^{-9} \text{ and antilog } 0.48 = 3.1$$

Therefore $$(H^+) = 3.1 \times 10^{-9}\ M$$

$$(H^+)(OH^-) = 1 \times 10^{-14}$$

$$(OH^-) = \frac{1 \times 10^{-14}}{(H^+)} = \frac{1 \times 10^{-14}}{3.1 \times 10^{-9}} = 3.2 \times 10^{-6}\ M$$

If $(OH^-) = 3.2 \times 10^{-6}\ M$, then (HAc) has the same value. The equilibrium expression for the hydrolysis reaction is

$$\frac{(HAc)(OH^-)}{(Ac^-)} = K_H = \frac{K_W}{K_I} = \frac{1 \times 10^{-14}}{1.85 \times 10^{-5}} = 5.4 \times 10^{-10}$$

Then

$$\frac{(HAc)(OH^-)}{(Ac^-)} = \frac{(3.2 \times 10^{-6})(3.2 \times 10^{-6})}{(Ac^-)} = 5.4 \times 10^{-10}$$

$$(Ac^-) = \frac{(3.2 \times 10^{-6})^2}{5.4 \times 10^{-10}} = \frac{10.2 \times 10^{-12}}{5.4 \times 10^{-10}} = 1.9 \times 10^{-2} \text{ mole per liter}$$

$$.019 \text{ mole per liter} = \frac{.019}{2} \text{ mole per 500 ml.} = .0095 \text{ mole per 500 ml.}$$

The molecular weight of NaAc is 82. Therefore, .0095 mole per 500 ml. is equivalent to $.0095 \times 82$ or 0.78 g. NaAc per 500 ml.

Example 6.

(a) What is the concentration of the H^+ ion and of the OH^- ion in a solution which is .05 M with respect to NH_4CN?

(b) What is the degree of hydrolysis of the NH_4CN?

Ammonium cyanide is a salt of a weak acid and of a weak base. Both ions undergo hydrolysis in accordance with the equation

$$NH_4^+ + CN^- + H_2O = NH_4OH + HCN$$

The equilibrium expression is

$$\frac{(NH_4OH)(HCN)}{(NH_4^+)(CN^-)} = K_H = \frac{K_W}{K_{I(base)} K_{I(acid)}} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 4 \times 10^{-10}}$$

$$K_H = \frac{1 \times 10^{-14}}{7.2 \times 10^{-15}} = 1.4$$

We shall assume that for every NH_4^+ ion which hydrolyzes, a CN^- ion also hydrolyzes. It can be shown readily that this assumption is a justifiable one provided the concentration of the NH_4CN is not exceedingly low. Let X be the number of moles of NH_4^+ ion undergoing hydrolysis; then X is also the number of moles of CN^- ion hydrolyzed. Since the initial concentration of the NH_4CN is .05 M and since the salt is completely ionized, the initial concentration of NH_4^+ ion and of CN^- ion is each .05 M. But at equilibrium, $(NH_4^+) = (.05 - X)$, and $(CN^-) = (.05 - X)$. Then

$$\frac{(NH_4OH)(HCN)}{(NH_4^+)(CN^-)} = \frac{X \times X}{(.05 - X)(.05 - X)} = \frac{X^2}{(.05 - X)^2} = 1.4$$

Taking the square root of both sides of the equation, we have

$$\frac{X}{.05 - X} = 1.18$$

$$X = .059 - 1.18X$$

$$2.18X = .059$$

$$X = .027 \text{ mole per liter} = (NH_4OH) = (HCN)$$

The value for the (H^+) may be calculated from the known amount of HCN produced and from the amount of CN^- ion remaining unhydrolyzed. The (HCN) was found to be .027 M; while the value for (CN^-) is $(.05 - X)$ or $(.05 - .027)$ or .023 M. The equation for the ionization of HCN is

$$HCN = H^+ + CN^-$$

while the equilibrium expression is

$$\frac{(H^+)(CN^-)}{(HCN)} = K_I = 4 \times 10^{-10}$$

Substituting in this expression the known values of (HCN) and (CN^-), we have

$$\frac{(H^+)(.023)}{.027} = 4 \times 10^{-10}$$

$$(H^+) = \frac{.027 \times 4 \times 10^{-10}}{.023}$$

$$(H^+) = 4.7 \times 10^{-10} \text{ mole per liter}$$

The (OH^-) then must be

$$(OH^-) = \frac{1 \times 10^{-14}}{4.7 \times 10^{-10}} = 2.1 \times 10^{-5} \text{ mole per liter}$$

The value for (OH^-) could have been calculated from the known amounts of NH_4OH and NH_4^+ ion present in the solution.

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

and

$$\frac{(NH_4^+)(OH^-)}{(NH_4OH)} = K_I = 1.8 \times 10^{-5}$$

Since (NH_4OH) has a value of .027 M and the (NH_4^+) a value of .023 M, then

$$\frac{.023(OH^-)}{.027} = 1.8 \times 10^{-5}$$

$$(OH^-) = \frac{.027 \times 1.8 \times 10^{-5}}{.023} = 2.1 \times 10^{-5} \text{ mole per liter}$$

This value is the same as that obtained in the first calculation.

The degree of hydrolysis is the number of moles of NH_4CN hydrolyzed divided by the total amount of NH_4CN originally present.

$$\text{Degree of hydrolysis} = \frac{X}{.05} = \frac{.027}{.05} = 0.54$$

$$\text{The percent hydrolysis} = 0.54 \times 100 = 54 \text{ percent}$$

Experiments show that the concentration of the H^+ ion in a solution of NH_4CN is the same for all concentrations of the salt, provided the concentration is not too high, in which case the Law of Mass Action fails to hold, and provided that the concentration of the salt is not excessively low, in which case the degree of hydrolysis of the NH_4^+ ion cannot be regarded as the same as that of the CN^- ion. At intermediate concentrations of NH_4CN the (H^+) is independent of the salt concentration and has a value which is determined by the values of the three equilibrium constants, namely, K_W, $K_{I(base)}$, and $K_{I(acid)}$. This relationship is

$$(H^+) = \sqrt{\frac{K_W \cdot K_{I(acid)}}{K_{I(base)}}}$$

We may arrive at this conclusion in the following manner. From the equilibrium expression for the ionization of HCN

$$\frac{(H^+)}{K_{I(acid)}} = \frac{(HCN)}{(CN^-)}$$

From the hydrolysis equilibrium we have

$$\frac{(NH_4OH)(HCN)}{(NH_4^+)(CN^-)} = \frac{K_W}{K_{I(base)} K_{I(acid)}}$$

But since $\frac{(NH_4OH)}{(NH_4^+)} = \frac{(HCN)}{(CN^-)}$, and since the latter expression $= \frac{(H^+)}{K_{I(acid)}}$,

we have $$\left(\frac{HCN}{CN^-}\right)^2 = \left(\frac{H^+}{K_{I(acid)}}\right)^2 = \frac{K_W}{K_{I(base)}\,K_{I(acid)}}$$

Then $$(H^+)^2 = \frac{K_W(K_{I(acid)})^2}{K_{I(base)}\,K_{I(acid)}}$$

$$(H^+)^2 = \frac{K_W K_{I(acid)}}{K_{I(base)}}$$

and $$(H^+) = \sqrt{\frac{K_W K_{I(acid)}}{K_{I(base)}}}$$

Substituting into this expression the values for the constants, we have

$$(H^+) = \sqrt{\frac{1 \times 10^{-14} \times 4 \times 10^{-10}}{1.8 \times 10^{-5}}} = 4.7 \times 10^{-10} \text{ mole per liter}$$

This value for the (H^+) is the same as that originally obtained directly from the hydrolysis equilibrium. It may be advantageous, as the occasion arises, to make use of this expression for calculating the concentration of the H^+ ion in a solution containing the salt of a weak acid and of a weak base.

Example 7.

Calculate the solubility of PbS in water:

(a) Neglecting the hydrolysis of the S^{--} ion.

(b) Considering the hydrolysis of the S^{--} ion.

The hydrolysis of the S^{--} ion becomes a very important factor in calculating the solubilities of sulfides from their solubility product constants and, conversely, in calculating the solubility product constants from solubility data. When hydrolysis is taken into account the solubility of any slightly soluble sulfide is about one thousand times greater than that calculated by neglecting hydrolysis.

(a) First calculate the solubility of PbS neglecting hydrolysis. ($K_{S.P.}$ for PbS $= 4 \times 10^{-26}$.)

$$PbS_{(s)} = Pb^{++} + S^{--}$$

Let X equal the number of moles of PbS dissolved in 1 liter of solution. Then X will be equal to (S^{--}) and (Pb^{++}).

$$(Pb^{++})(S^{--}) = X^2 = 4 \times 10^{-26}$$

$$X = 2 \times 10^{-13} \text{ mole per liter}$$

Therefore, the calculated solubility of PbS in water is 2×10^{-13} M if the hydrolysis of the S^{--} ion is neglected.

(b) In considering the hydrolysis of the S^{--} ion we can assume that only the first step of hydrolysis is important, since the second step is negligibly small.

$$S^{--} + H_2O = HS^- + OH^-$$

The value for K_H for this reaction as calculated previously in *Example 3* is .077, and we found the S^{--} ion to be hydrolyzed to the extent of 58 percent in 0.1 M Na_2S solution. At lower concentrations the hydrolysis of the S^{--} ion is even greater than this. If the concentration of the S^{--} ion were extremely small, of the order of magnitude of the concentration of the OH^- ion in water, then the hydrolysis would be reduced somewhat due to the common ion effect of the OH^- ion. Nevertheless, the S^{--} ion at a concentration of 1×10^{-13} M would be practically completely hydrolyzed. In such an event the concentration of the OH^- ion produced by the hydrolysis would be only 1×10^{-13} M. This value is small compared with the concentration of the OH^- ion already present in water, namely, 1×10^{-7} M. Therefore, though the hydrolysis of the S^{--} ion in a saturated solution of PbS may be complete, the (OH^-) in the solution will still have a value of 1×10^{-7} M. Accordingly,

$$\frac{(HS^-)(OH^-)}{(S^{--})} = \frac{(HS^-) \times 1 \times 10^{-7}}{(S^{--})} = K_H = .077$$

$$\frac{(HS^-)}{(S^{--})} = 7.7 \times 10^5 \quad \text{or} \quad (S^{--}) = \frac{(HS^-)}{7.7 \times 10^5}$$

From this ratio we see that there are almost one million times as many HS^- ions as S^{--} ions in solution and that the hydrolysis is almost complete. From the two equilibria involved here

$$PbS_{(s)} = Pb^{++} + S^{--}$$
$$S^{--} + H_2O = HS^- + OH^-$$

it is evident that for every S^{--} ion which is removed by hydrolysis, one Pb^{++} ion and one HS^- ion are produced. Therefore, the concentration of the Pb^{++} ion will be practically the same as the concentration of the HS^- ion in solution.

Substituting the value for the S^{--} ion concentration in the solubility product expression, we have

$$(Pb^{++})(S^{--}) = (Pb^{++})\frac{(HS^-)}{7.7 \times 10^5} = K_{S.P.} = 4 \times 10^{-26}$$

Since $(Pb^{++}) = (HS^-)$,

$$\frac{(Pb^{++})^2}{7.7 \times 10^5} = 4 \times 10^{-26}$$

$$(Pb^{++})^2 = 3.1 \times 10^{-20}$$

$$(Pb^{++}) = 1.8 \times 10^{-10} \text{ mole per liter}$$

Therefore, the solubility of PbS in 1 liter of solution is also 1.8×10^{-10} mole per liter, which value is approximately one thousand times greater than that obtained (2×10^{-13} M) when hydrolysis is neglected.

If we were to consider the second step of hydrolysis,

$$HS^- + H_2O = H_2S + OH^-$$

the calculated solubility would be further increased but the order of magnitude of the solubility would not be appreciably changed. In addition, the Pb^{++} ion undoubtedly hydrolyzes to give $Pb(OH)^+$ ion and $Pb(OH)_2$, and these effects would also increase the solubility of PbS.

Example 8.

Calculate the concentration of (a) the H^+ ion, (b) the OH^- ion, (c) the HCO_3^- ion, and (d) the CO_3^{--} ion in a solution which contains 0.1 mole of $NaHCO_3$ per liter.

Since $NaHCO_3$ is a salt it is completely ionized to give Na^+ and HCO_3^- ions. The HCO_3^- ion is not only a weak acid itself but it is also an ion of another weak acid, H_2CO_3. Therefore, the HCO_3^- ion takes part in two reactions in water solution,

$$HCO_3^- + H_2O = H_2CO_3 + OH^- \qquad (1)$$

and

$$HCO_3^- = CO_3^{--} + H^+ \qquad (2)$$

Reaction (1), the hydrolysis of the HCO_3^- ion, produces OH^- ion, while reaction (2), the ionization of the HCO_3^- ion, produces H^+ ion. As both reactions proceed, the H^+ and OH^- ions formed are practically all used up in the formation of water,

$$H^+ + OH^- = H_2O \qquad (3)$$

Adding equations (1), (2), and (3), we have

$$2HCO_3^- = H_2CO_3 + CO_3^{--} \tag{4}$$

The equilibrium expression for (4) is

$$\frac{(H_2CO_3)(CO_3^{--})}{(HCO_3^-)^2} = K_{(4)}$$

When equations are added, the corresponding equilibrium expressions are multiplied. Therefore the numerical value for $K_{(4)}$ is

$$\frac{(H_2CO_3)(OH^-)}{(HCO_3^-)} \times \frac{(CO_3^{--})(H^+)}{(HCO_3^-)} \times \frac{1}{(H^+)(OH^-)} = K_{(1)} \times K_{(2)} \times K_{(3)}$$

Cancelling (H^+) and (OH^-) in the numerator and denominator,

$$\frac{(H_2CO_3)(CO_3^{--})}{(HCO_3^-)^2} = K_{(1)} \times K_{(2)} \times K_{(3)} = K_{(4)}$$

$K_{(1)}$ is the hydrolysis constant for the HCO_3^- ion and has a value of $\frac{1 \times 10^{-14}}{4.2 \times 10^{-7}}$; $K_{(2)}$ is the ionization constant for the second stage of ionization of carbonic acid and is equal to 4.8×10^{-11}; and $K_{(3)}$ equals $\frac{1}{K_W}$ or $\frac{1}{1 \times 10^{-14}}$. Substituting these values in the above expression, we have

$$\frac{(H_2CO_3)(CO_3^{--})}{(HCO_3^-)^2} = \frac{1 \times 10^{-14}}{4.2 \times 10^{-7}} \times \frac{4.8 \times 10^{-11}}{1} \times \frac{1}{1 \times 10^{-14}}$$

$$= 1.14 \times 10^{-4} = K_{(4)} \tag{5}$$

Referring to equations (1), (2), and (3), it is seen that for every OH^- ion which reacts with H^+ ion to form water, one H_2CO_3 molecule and one CO_3^{--} ion are produced. Therefore, for practical purposes we are justified in making the assumption that at equilibrium the (H_2CO_3) will be the same as the (CO_3^{--}). We can also assume that since reactions (1) and (2) take place to a limited extent, the (HCO_3^-) remains practically unchanged; therefore, in this case the value for (HCO_3^-) will be for all practical purposes 0.1 *M*.

Making use of equation (5) and letting (H_2CO_3) and (CO_3^{--}) each be X, we have

$$\frac{X^2}{(0.1)^2} = 1.14 \times 10^{-4}$$

$$X^2 = 1.14 \times 10^{-6}$$

$$X = 1.06 \times 10^{-3} \text{ mole per liter} = (H_2CO_3) = (CO_3^{--})$$

Having obtained the values for (H_2CO_3) and (CO_3^{--}), (H^+) and (OH^-) may then be calculated from the equilibrium expressions of (1) and (2). Taking reaction (2), we have

$$\frac{(H^+)(CO_3^{--})}{(HCO_3^-)} = \frac{(H^+) \times 1.06 \times 10^{-3}}{0.1} = K_{(2)} = 4.8 \times 10^{-11}$$

$$(H^+) = \frac{0.1 \times 4.8 \times 10^{-11}}{1.06 \times 10^{-3}} = 4.5 \times 10^{-9} \text{ mole per liter}$$

The value for (OH^-) may then be obtained from the water equilibrium as follows.

$$(OH^-) = \frac{1 \times 10^{-14}}{4.5 \times 10^{-9}} = 2.2 \times 10^{-6} \text{ mole per liter}$$

The $NaHCO_3$ solution is found to be basic.

The value for the concentration of the hydrogen ion in this solution may be obtained more conveniently by making use of a general rule which can readily be shown to hold for acid salts of the type $NaHCO_3$. The rule states that the (H^+) is equal to the square root of the product of the two ionization constants for the dibasic acid. Thus, in the present case,

$$(H^+) = \sqrt{K_{I_1} \times K_{I_2}}$$

$$(H^+) = \sqrt{4.2 \times 10^{-7} \times 4.8 \times 10^{-11}}$$

$$(H^+) = \sqrt{20 \times 10^{-18}}$$

$$(H^+) = 4.5 \times 10^{-9} \text{ mole per liter}$$

This value is the same as that obtained in the previous calculation. Since the latter calculation does not involve the concentration of the dissolved $NaHCO_3$, the value obtained for (H^+) must be the same for all concentrations of the salt.

The rule, in this case, may be derived from the first and second ionization constants for carbonic acid.

$$\frac{(H^+)^2(CO_3^{--})}{(H_2CO_3)} = K_1 \times K_2$$

Remembering that for all practical purposes (CO_3^{--}) and (H_2CO_3) are essentially the same, we therefore cancel them in the above expression, and

$$(H^+) = \sqrt{K_1 \times K_2}$$

At intermediate concentrations, this relationship applies to such ions of weak acids as $HC_2O_4^-$, $H_2PO_4^-$, $H_2PO_3^-$, HSO_3^-, and HS^-.

Questions and Problems

1. Write the equation representing the dissociation of water into H^+ and OH^- ions. Explain why the addition of more water will not shift this equilibrium. How may it be shifted?
2. Why is the equilibrium expression for the dissociation of water written $(H^+) \times (OH^-)$ and not $\frac{(H^+) \times (OH^-)}{(H_2O)}$?
3. When solid sodium acetate is added to water why do not all of the Ac^- ions combine with H^+ ions to form acetic acid?
4. Does (a) the salt of a weak acid and a strong base, (b) the salt of a strong acid and a weak base, (c) the salt of a strong acid and a strong base, produce an acidic, basic or neutral solution?
5. Show that the hydrolysis constant for a salt of a strong base and a weak acid is equal to the ionization constant for water divided by the dissociation constant for the acid.
6. Show that the hydrolysis constant for the ***first*** step of hydrolysis for the salt of a strong base and a weak dibasic acid is equal to the ionization constant for water divided by the second dissociation constant for the acid.
7. Explain why aluminum hydroxide and not aluminum carbonate is precipitated from solution when a solution of sodium carbonate is added to one of aluminum sulfate.
8. Why is BaS not stable when added to water?
9. Why is the carbonate ion concentration in a solution of ammonium carbonate less than it is in a sodium carbonate solution of the same molarity?
10. Explain by the Rule of Le Chatelier why the degree of hydrolysis of sodium acetate increases as the solution is diluted.
11. Write equations for the hydrolysis reactions occurring when sodium carbonate is dissolved in water.
12. If a 0.1 molar solution of HCN is neutralized by a 0.1 molar solution of NaOH the two solutions do not neutralize each other when the H^+ ion concentration is 10^{-7} molar but rather when the H^+ concentration is about 10^{-11} molar. Explain.
13. What is a buffer solution? Explain its action.
14. Write the ionic equations for the reaction representing the hydrolysis of each of the following salts:
    (a) Ammonium chloride — NH_4Cl
    (b) Sodium acetate — $NaC_2H_3O_2$

(c) Methyl ammonium chloride — CH_3NH_3Cl
(d) Sodium benzoate — $NaC_6H_5CO_2$
(e) Potassium cyanide — KCN
(f) Sodium phenolate — NaC_6H_5O
(g) Barium nitrite — $Ba(NO_2)_2$
(h) Lithium formate — $LiCHO_2$
(i) Dimethyl ammonium chloride — $(CH_3)_2NH_2Cl$
(j) Potassium propionate — $KC_3H_5O_2$

15. Calculate the hydrolysis constant for each of the salts listed in problem 14. (K_I for the corresponding acids or bases are given in tables in the Appendix.)

16. Calculate the (H^+) for (A) a 0.1 molar, (B) a .01 molar solution of each of the salts listed in problem 14.

17. What is the *p*H value for each of the solutions in problem 16?

18. What is the degree of hydrolysis for each salt in problem 16?

19. How many grams of sodium acetate must be added to 1 liter of water to give an OH^- ion concentration of 1×10^{-5} mole per liter?

20. How many grams of NH_4Cl must be added to 1 liter of water to give an OH^- ion concentration of 10^{-9} mole per liter?

21. How many moles of NH_4Cl must be added to 1 liter of water to give the same *p*H value as a 0.1 molar solution of HCN?

22. (a) Using only K_I(HAc), calculate the H^+ concentration in a solution containing 0.1 mole sodium acetate and 0.1 mole acetic acid. (b) Repeat the calculation using K_H.

23. What is the concentration of the undissociated HAc in a solution containing 1 mole NaAc per liter?

24. A .01 molar solution of NaCN is found to be hydrolyzed to the extent of 5 percent. What is the value of the ionization constant for HCN?

25. Show by calculation whether it is possible to make a solution of sodium formate concentrated enough to produce the same OH^- concentration as that of a .001 molar solution of KCN. (In this case assume the Law of Mass Action to hold for concentrated solutions.)

26. Calculate (a) the hydrolysis constant, (b) the H^+ ion concentration, and (c) the degree of hydrolysis for a 0.1 *M* Na_2CO_3 solution. (Neglect the second hydrolysis step.)

27. What will be the minimum concentration of a NaAc solution necessary to begin the precipitation of $Mg(OH)_2$ if equal quan-

tities of this solution and one containing 0.2 mole Mg^{++} ion per liter are mixed?

28. Solid Na_2S is added slowly to a .01 *M* $FeSO_4$ solution. Which will be precipitated first, $Fe(OH)_2$ or FeS?

29. Calculate the H^+ ion concentration in the resulting solution when equal amounts of the following are mixed:
(a) 0.1 *M* HCl and 0.1 *M* NH_4OH
(b) 0.1 *M* HCl and 0.1 *M* NaOH
(c) 0.1 *M* H_2SO_4 and 0.1 *M* NaOH (see p. 181)
(d) .02 *M* HAc and .02 *M* NaOH
(e) 0.1 *M* H_2S and 0.2 *M* NaOH

30. Calculate the CO_3^{--} ion concentration and the OH^- ion concentration in a .01 *M* solution of $NaHCO_3$. (See *Example 8*, page 238.)

31. If $MgCl_2$ is added slowly to a solution which is 0.1 *M* with respect to $NaHCO_3$, which will begin to precipitate first, $Mg(OH)_2$ or $MgCO_3$? (See *Example 8*, page 238.)

32. Calculate the solubility in moles per liter of the following sulfides in water, (A) neglecting the hydrolysis of the S^{--} ion, (B) considering the hydrolysis of the S^{--} ion.
(a) CdS (b) CuS (c) PbS (d) Ag_2S (e) CoS

33. What must be the ratio of (Ac^-) to (HAc) in a buffer solution made up of acetic acid and sodium acetate if the H^+ ion concentration is to be maintained at 10^{-5} *M*?

34. What is the concentration of the H^+ ion in a solution which is .01 *M* with respect to $ZnCl_2$? ($K_I(Zn(OH)^+$ has a value of 4×10^{-5}.)

35. Calculate the ratio of the (HPO_4^{--}) to $(H_2PO_4^-)$ in a solution in which these two ions are used as a buffer, if the *p*H of the solution is to be maintained at (a) 6.0, (b) 7.0, and (c) 8.0. Assume that the H^+ ion concentration is controlled entirely by the reaction $H_2PO_4^- = H^+ + HPO_4^{--}$.

CHAPTER

11

Complex Ions

For the sake of simplicity and because of a lack of definite information we designate an ion in solution merely by the symbol of the element or radical and by the charge which the ion carries. Thus, hydrogen ion is written as H^+; sodium ion, Na^+; chloride ion, Cl^-; sulfate ion, SO_4^{--}, etc. There is sufficient evidence for the argument that no ion exists in solution as a simple charged atom or group as its chemical symbol might imply. It has been shown by experiments designed to determine the relative amounts of electricity carried by various ions in solution that ions carry with them relatively large quantities of water. Although it is not possible as yet to determine the absolute amount of water carried by each, these experiments do allow calculations to be made concerning the amount of water carried by an ion of one element or group, relative to that transported by an ion of another element or group. For example, if we arbitrarily assume that the fastest moving ion, the hydrogen ion, carries a minimum amount of water, one molecule, then the potassium ion carries on the average about five; the sodium ion, eight; the lithium ion, fourteen; while the chloride ion carries about four molecules of water. These numbers are known as the *hydration numbers* of the ions. These hydration numbers vary with the concentration of the solution. They are related to the speeds of the ions, in that an ion carrying a large amount of water moves

slowly in comparison with an ion which carries a relatively small amount of water.

From what has been said in earlier chapters regarding the attractive forces between ions of opposite charge, it would seem reasonable to expect that these attractive forces also exist between ions and water molecules to give rise to hydrated ions, since the water molecule is a dipole having separated positive and negative centralizations of charge. Polar molecules tend to attract each other to form aggregates of molecules and, similarly, we might conclude that polar water molecules are attracted to charged ions in solution. Accordingly, we may look upon all ions as solvated in solution, i.e., having molecules of solvent attached to them.

The union between most ions and water is not a very firm or stable one, and the law of definite proportions does not apply in the cases cited, namely, the hydration of such ions as Li^+, Na^+, and Cl^-. The binding force between water molecules and these ions is of the dipole moment type. The sodium ion, for example, attracts the negative end of the water molecule, thus binding the water molecule to it. If one were able to see these hydrated molecules with a sub-microscopic eye, he would find that some sodium ions have six H_2O molecules associated with them; some, seven; some, eight; others, nine; etc. The average number would be about eight.

In the case of the cobalt ion, however, a definite number of water molecules are associated with each metallic cobalt ion. This definiteness in the number of water molecules associated with the cobalt ion indicates that the bonding is primarily of the covalent type, i.e., by shared electrons. When we speak of complex ions we usually are referring to the coordinately bonded, exactly defined type of ion. Examples of such complex ions involving other than H_2O molecules are: $Zn(NH_3)_4^{++}$, $Fe(CN)_6^{---}$, $AgCl_2^-$, and $Co(NH_3)_6^{+++}$.

It is possible to produce complex ions which are made up of a positively charged metallic ion and more than one kind of negative ion or neutral molecule associated with it. For example, the following complex molecules or ions are known:

$[Co(NH_3)_3\,Cl_3]$, $[Co(NH_3)_2\,Cl_4]^-$, $[Co(NH_3)_4\,Cl_2]^+$, etc. (in all combinations). Note that, for the first example given, the charge on the ion is zero; it is a neutral molecule. The charge on the next ion is -1 (it is an anion), and for the third, $+1$ (a cation). Thus complex ions made up from positively charged metallic ion cores are not necessarily positively charged. They may be neutral molecules, anions, or cations.

The Hydronium Ion. Since the hydrogen ion moves much faster than any other ion in solution when subjected to an electric field, we believe that it has associated with it less water than other ions. If we assume that it combines with one molecule of water, we may write its formula as $H^+(H_2O)$ or H_3O^+.

$$H^+ + H_2O = H_3O^+ \qquad (1)$$

The latter ion is known as the ***hydronium ion*** and is believed by many to represent the condition of the hydrogen ion in water.

One argument for this structure for the H^+ ion in water is that the H_2O molecule possesses an extra pair of bonding p electrons which are available to combine with the H^+ ion. This process is illustrated schematically in Figure 11.1.

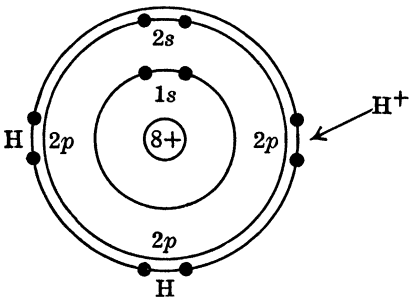


FIG. 11.1 The electronic concept of the formation of the H_3O^+ ion.

The H_3O^+ ion thus formed can have other H_2O molecules attached to it through the action of dipole forces. Only one H_2O molecule is associated with the H^+ ion in the form of a covalent bond. Other arguments for believing that the H^+ ion exists in water solution as H_3O^+ are given in the following paragraphs.

When two substances react with each other to form a third substance, an energy change takes place which usually manifests itself in the form of heat; heat is either liberated or ab-

sorbed. The former is the more usual case. This heat effect is usually large when the substance formed possesses great stability. In general, the smaller the heat effect the less stable is the product. When one substance dissolves in another, an energy change likewise results. Heat is usually, not always, absorbed in the process of solution, but the magnitude of the energy change is usually very small compared with that involved in a chemical reaction. When HCl, H_2SO_4, HBr, HNO_3, and similar substances are placed in water a very large amount of heat is liberated, much more than one would expect from the simple process of solution. On the contrary, when sodium chloride is placed in water, a small amount of heat is absorbed. Many other salts behave similarly. Where the hydrogen ion is involved in the process of solution, the amount of heat liberated is comparable with that of many chemical reactions. This behavior may be ascribed to the formation of the hydronium ion.

If we assume that one molecule of water is associated with the hydrogen ion, the resulting hydronium ion may be represented structurally as being similar to the ammonium ion. The hydronium ion is a complex ion and is the fundamental particle used in the Brønsted definitions for the explanation of acid-base reactions.

The Ammonium Ion. Pure liquid ammonia, boiling point −33.5° C, is a poorer conductor of electricity than is pure water; the conductivity of water is at least 10,000 times greater than that of ammonia. When hydrogen chloride is placed in pure ammonia the resulting solution is found to be an excellent conductor of electricity; the value of its conductivity is of the same order of magnitude as that of hydrogen chloride in water. In this case a reaction takes place which involves the formation of a new ion. The ion produced is quite familiar to us, the ammonium ion, and its formation may be expressed by the equation,

$$H^+ + NH_3 = NH_4^+ \qquad (2)$$

The ammonium ion is a complex ion and may be looked upon as an analogue of the hydronium ion. It differs from the

hydronium ion in that it forms salts with negative ions which possess considerable stability. When the excess ammonia from the solution just considered is allowed to evaporate, a solid remains which upon examination is found to be ammonium chloride. It is known that solid ammonium chloride may be heated to several hundred degrees before it noticeably dissociates to give ammonia and hydrogen chloride. Ammonia reacts in a similar manner with many other hydrogen compounds; thus HBr, HI, H_2SO_4, and HNO_3 form ammonium salts with ammonia, all of which are highly stable in that they may be crystallized from solution.

Pure ammonia ionizes very slightly in accordance with the equation,

$$NH_3 = H^+ + NH_2^- \tag{3}$$

The hydrogen ion formed in this process combines with ammonia, as expressed in equation (2). The NH_2^- (amide) ion in liquid ammonia corresponds to the OH^- ion in water, and metal ions in combination with the NH_2^- ion behave as bases.

Like hydrogen chloride in water (hydronium chloride), ammonium chloride behaves as an acid in liquid ammonia. It will react with ammono bases such as potassium amide, KNH_2, sodium amide, $NaNH_2$, etc., to form salts and ammonia. These reactions are analogous to those between hydrochloric acid and hydroxides in water. Typical reactions in the two solvents may be written:

$$H_3O^+ + OH^- = 2H_2O \tag{4}$$

$$NH_4^+ + NH_2^- = 2NH_3 \tag{5}$$

One of the characteristic properties of an acid in an aqueous medium is its ability to react with certain metals with the displacement of hydrogen. Thus,

$$Zn + 2H^+ = Zn^{++} + H_2 \tag{6}$$

or, using hydronium chloride,

$$Zn + 2H_3O^+ = Zn^{++} + H_2 + 2H_2O \tag{7}$$

Ammonium chloride in liquid ammonia behaves in a similar manner,

$$Zn + 2NH_4^+ = Zn^{++} + H_2 + 2NH_3 \qquad (8)$$

Like the hydronium ion in water, the ammonium ion in ammonia is an acid. The only essential difference between the two is that the ammonium ion possesses a far greater stability at ordinary temperatures than does the hydronium ion. The similarity of water to ammonia leads to the assumption of the hydronium ion as the analogue of the ammonium ion. However, for most purposes it is immaterial which formula we use. Simplicity recommends the use of the symbol H^+ rather than H_3O^+ for the hydrogen ion in water solution.

Solid Hydrates and Ammonates. The ability of ions to combine with water and ammonia molecules is not limited to the hydrogen ion. As we previously stated, attractive forces exist between ions and polar water molecules, and all ions are more or less associated with water in this medium. In most cases the resulting combination, which is not a definite one, is capable of existence only in solution. Sometimes a crystalline product containing water may be obtained from solution. The number of such compounds is relatively large; only a few familiar examples may be mentioned here, such as $CuSO_4 \cdot 5H_2O$, $CaCl_2 \cdot 6H_2O$, $Na_2SO_4 \cdot 10H_2O$, and $CrCl_3 \cdot 6H_2O$. These addition compounds, made up of salts and water molecules, are commonly called ***hydrates.*** The fact that these solids contain water in definite proportions is no assurance that definite proportions hold true in solution. The crystal lattice, i.e., the space distribution in the crystal, allows a definite number of water molecules to be associated or trapped with each particle (ion or atom) in the crystal. Such restrictions do not prevail in solution.

Ammonia shows an even greater tendency to combine with ions both in water and in liquid ammonia to form analogous solid compounds, called ***ammonates.*** Characteristic examples of such combinations are $CuSO_4 \cdot 4NH_3$, $CaCl_2 \cdot 8NH_3$, $CrCl_3 \cdot 6NH_3$, and $CoCl_3 \cdot 6NH_3$. All of these ammonates may

be crystallized from solution and upon analysis they have been shown to be definite compounds. In general, the ammonates are more stable, both in solution and in the solid state, than are the analogous combinations containing water molecules. This property of ions or molecules to combine with solvent molecules is not confined entirely to water and ammonia. Molecules of many other solvents show the same tendency to a greater or lesser degree. This fact is demonstrated clearly when one considers that there are known in well-crystallized form several thousand combinations similar to those mentioned above, in which water, ammonia, alcohols, amines, and many other solvent molecules assume a definite part in the crystalline solid complex.

Valence and Complex Molecules. An examination of complex molecules reveals that the valence relationships among their atoms cannot be explained by the ordinary concepts which apply fairly well to other types of molecules. It appears that in each instance the ion in the complex molecule exhibits a combining capacity which exceeds the primary or ordinary valence. Thus in $[Cu(NH_3)_4]^{++}$ the copper ion displays the ability to acquire four additional molecules of ammonia. On the other hand, the cobalt ion takes on six molecules of water or ammonia. A similar situation exists in many other known compounds. This additional combining capacity is usually spoken of as the ***auxiliary*** or ***secondary valence,*** which for the copper ion is four and for the cobalt ion, six. What is the nature of this auxiliary valence and what explanation can be offered to account for it?

In an earlier chapter we considered the electronic structures of atoms and molecules and on this basis explained the difference between the main and sub-groups of the periodic system. It is the elements of the sub-groups, with their shells of 18 rather than 8 electrons in the next to their outermost shells, that we shall now consider with respect to the formation of complex ions and molecules.

When the periodic table is followed into the third series of elements (beginning with argon), scandium appears in the

third group. This element is not very closely related to the preceding elements in the same group. Since it is in the first long series, between argon and krypton, which series is composed of 18 elements, a shell of 18 electrons must be taken into consideration. In the case of scandium one electron falls back into a shell which already possesses a stable grouping of eight electrons; this shell then contains nine electrons (see p. 82). This is the first step in the formation of an inner shell of 18 electrons. The same shell for the element titanium (atomic number 22, one greater than that of scandium) contains 10 electrons, for vanadium it contains 11 electrons, etc., until zinc (atomic number 30) is reached, which has 18 electrons. This number persists in this shell as far as the next rare gas, krypton (atomic number 36). The fourth series of the periodic table is likewise a long series and contains 18 elements, while the fifth series contains 32 elements, due to the 14 rare earth elements which occupy a single position in the table. The elements in these long series have more than 8 electrons in the next to the outermost shell. The outermost shell contains the normal valence electrons. In the long series we find the elements which make up the sub-groups of the table and, in addition, the transition elements, such as iron, cobalt and nickel.

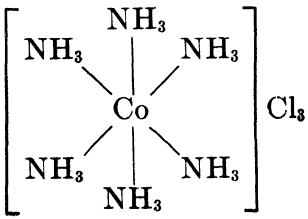
Ions which show no auxiliary valence have a completed group of eight electrons in the outermost shell. Those displaying secondary valence have in their outermost shells either a completed or partially completed group of 18 electrons. Thus, the magnesium ion (magnesium atom minus 2 electrons) has an outer group of 8 electrons while the zinc ion has an outer group of 18.

The secondary valence which is displayed in the formation of complex molecules is undoubtedly due to forces which result from the electrons of that shell immediately within the one containing the valence electrons of the atoms, i.e., the outermost shell of the ions. The binding between the metal ion and the peripherally attached molecules or ions is probably of the coordinately bonded type. This fact is strongly suggested when one considers the properties of these complexes. (We

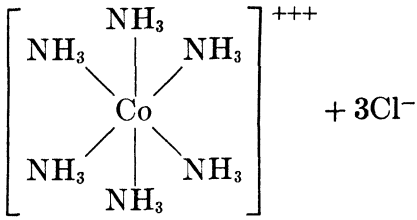
shall consider the electronic structures of complex ions in a later section of this chapter.)

The Coordination Theory of Werner. About the beginning of the century, Alfred Werner, a German chemist, made a thorough study of complex molecules and proposed a theory which fits their observed properties in a remarkable manner. He first introduced the concept of auxiliary or secondary valence, thus explaining the behavior of these compounds. Let us examine this theory in order to explain the properties of a typical complex molecule such as $CoCl_3 \cdot 6NH_3$. This molecule is a salt, a good conductor of electricity in water solution, and its anion may readily be identified as the chloride ion by the precipitation of silver chloride when silver nitrate is added to its solution. All the chlorine is found in the anion form, and sulfuric acid converts the complex into the corresponding sulfate salt. Contrary to what might be expected, sulfuric acid fails to remove ammonia molecules very rapidly from the complex, even though ammonia and hydrogen ion have a great tendency to combine with each other to form the ammonium ion, NH_4^+.

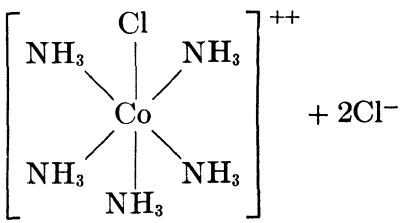
This complex ion is not as stable as one might think. The dissociation constant for the equilibrium, $Co(NH_3)_6^{+++} = Co^{+++} + 6NH_3$, has a value of 2.2×10^{-34}; however, the Co^{+++} ion appears to the first power and the concentration of NH_3 to the sixth power. (These high powers or exponents make the equilibrium constant seem inordinately small.) On standing, dissociation becomes appreciable; it so happens that the rate of dissociation is low, which effect makes it appear that the complex is much more stable than it actually is. On the basis of these properties and according to the theory of Werner the molecule is represented as $[Co(NH_3)_6]Cl_3$, or



It is assumed that the addition of the six molecules of ammonia takes place through the secondary valencies. The complex grouping contains only a cobalt atom and ammonia molecules, and as a unit it does not possess properties characteristic of either constituent. The chlorine atoms, however, retain their characteristic properties, in that all three are readily removed by silver ions with the formation of silver chloride. Consequently, all three chlorine atoms must exist in solution as chloride ions. The conductivity of this complex in water solution has a value similar to that of a typical tri-univalent electrolyte such as ferric chloride, $FeCl_3$; hence the complex must produce four ions. Accordingly, we may indicate its structure in solution as



One molecule of ammonia may be easily removed from the cobalt complex discussed above by heating the solid to 250° C. This procedure produces the compound $CoCl_3 \cdot 5NH_3$. When this molecule is treated with silver ion in water solution, only two chlorine atoms are readily removed through the precipitation of silver chloride. In addition, the conductivity of this salt shows it to be a bi-univalent electrolyte, producing only three ions. Its structure may be represented as



In like manner $[Co(NH_3)_4Cl_2]Cl$ is found to be a uni-univalent electrolyte, because of its conductivity and because

silver ion reacts rapidly with only one chloride ion per molecule. $[Co(NH_3)_3Cl_3]$ is quite insoluble in water and is a nonconductor of the electric current. Silver ion fails to precipitate silver chloride rapidly when added to a solution of this compound. Continued removal of ammonia and the addition of potassium nitrite produces $K[Co(NH_3)_2(NO_2)_4]$, which is found to be a uni-univalent electrolyte and to ionize as

$$K[Co(NH_3)_2(NO_2)_4] = K^+ + [Co(NH_3)_2(NO_2)_4]^- \qquad (9)$$

The resulting charge on the complex ion is negative because the nitrite ions replacing the ammonia molecules in the complex are themselves negatively charged. By this process a neutral molecular complex is changed into a negatively charged ion.

The resulting charge on any complex ion can easily be determined by taking the algebraic sum of the charges on the constituent parts of the complex ion. Thus, in this case,

Co^{+++} contributes 3 +
$2NH_3$ contribute 0
$4NO_2^-$ contribute 4 −
resultant charge 1 −

The next member of the series is not known, but its formula would be $K_2[Co(NH_3)(NO_2)_5]$, a uni-bivalent electrolyte. The last member of the series is well known as potassium cobaltinitrite which is only slightly soluble in water. In one of the analytical tests for potassium ion, the sodium salt, $Na_3[Co(NO_2)_6]$, is added to a solution of the unknown. In dilute solution $NaK_2[Co(NO_2)_6]$ is precipitated if potassium ion is present; in concentrated solution $K_3[Co(NO_2)_6]$ may be formed. The latter is a uni-trivalent electrolyte, as shown by the magnitude of its conductivity, and ionizes in solution to produce four ions,

$$K_3[Co(NO_2)_6] = 3K^+ + [Co(NO_2)_6]^{---} \qquad (10)$$

The following series of platinum compounds is also well established: $[Pt(NH_3)_6]Cl_4$, $[Pt(NH_3)_5Cl]Cl_3$, $[Pt(NH_3)_4Cl_2]Cl_2$, $[Pt(NH_3)_3Cl_3]Cl$, $[Pt(NH_3)_2Cl_4]$, $[Pt(NH_3)Cl_5]K$, and

$[PtCl_6]K_2$. It will be observed that the number of single constituents associated with the central atom in the complex cation or anion, as the case may be, in both the cobalt and platinum series, is always six. This number is known as the ***coordination number,*** which for most ions is usually 4 or 6. In the case of the well-known copper-ammonia complex ion, $[Cu(NH_3)_4]^{++}$, the coordination number of the copper is 4.

The coordination number of an ion in many instances is equal to twice the charge on the ion. Thus the coordination number of Cu^{++} is 4; that of Zn^{++}, 4; that of Ag^{+}, 2; that of Cu^{+}, 2; and that of Co^{+++}, 6. This rule is not a rigid one; the most common exception is the coordination number of 6 for Fe^{++} in the ferrocyanides.

The complex anion or cation or molecule is sometimes designated as the ***coordination sphere.*** Thus the coordination sphere of the compound $[Co(NH_3)_5Cl]Cl_2$ contains one cobalt atom, five molecules of ammonia and one chlorine atom. Polyvalent acid radicals, such as SO_4^{--}, CO_3^{--}, $C_2O_4^{--}$ (oxalate) ions, may be taken up by the central atom and occupy two positions in the coordination sphere; for example, in the complex $[Co(NH_3)_4SO_4]Cl$, the coordination number of the cobalt ion remains as 6. Although the examples given above for the cobalt and platinum series contain only ammonia molecules, it must be remembered that water and other solvent molecules can occupy positions within the coordination sphere. The ammonia complexes are chosen here since they are well defined and relatively simple.

The following list includes some of the molecules and ions which form complexes with metallic cations:

NH_3, RNH_2, R_2NH, R_3N
H_2O, ROH, R_2O
CO, NO
CN^-, SCN^-, F^-, OH^-, Cl^-, Br^-, I^-

(The symbol R refers to an organic radical)

The student is very probably familiar with some of the complexes formed with negative ions, such as: ferricyanide ion,

$Fe(CN)_6^{---}$; ferrocyanide ion, $Fe(CN)_6^{----}$; aurous cyanide ion, $Au(CN)_2^-$, formed in the extraction of gold by the cyanide process; nickel carbonyl, $Ni(CO)_4$, an intermediate compound in the extraction and purification of nickel; and $Ag(Cl_2)^-$.

The Geometrical Configurations of Complex Ions. Previously we indicated schematically the structure of the $[Co(NH_3)_6]^{+++}$ ion as lying in one plane. Actually the distribution of the NH_3 molecules about the (Co^{+++}) core is that of an octahedron. In fact, all complex ions with a coordination number of 6 have octahedral structures. The octahedral structure of $[Co(NH_3)_6]^{+++}$ is that given in Figure 11.2

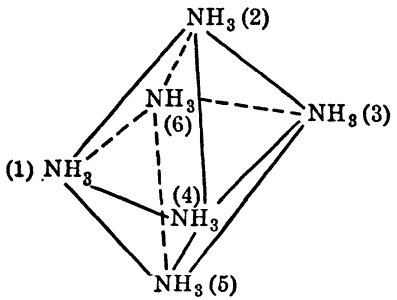


FIG. 11.2 The octahedral structure of the $Co(NH_3)_6^{+++}$ ion.

The Co^{+++} core lies within the octahedron. All edges of the octahedron have equal lengths. Suppose that we substitute two of the NH_3 groups by Cl^- ions. It will be apparent that substituting the Cl^- ions in positions 1 and 2 will result in the same configuration as in 1 and 4, 1 and 5, 1 and 6, 2 and 3, 2 and 4, 2 and 6, 3 and 4, 3 and 5, 3 and 6, 4 and 5, and 5 and 6. In each of the above cases one gets the same configuration by twisting the molecule around.* However, if the two Cl^- ions occupy positions 1 and 3, they are different from those cited above, but exactly like those configurations in which the Cl^- ions occupy positions 4 and 6, and 2 and 5. There are therefore two kinds of $[Co(NH_3)_4(Cl_2)]^+$ ions. The former are known as the *cis* and the latter as *trans* forms. These two different kinds of compounds have been isolated and shown to be different. The fact that two different compounds and no more than two are known confirms the octahedral structure of cobalt complexes and, in fact, all complexes with a coordi-

* Note that this twisting-of-the-molecule viewpoint does not apply in the case of resonance. With resonance the electron is conceived of being in both positions at the same time, or oscillating so fast as to be practically in this condition.

nation number of 6. These complex ions or compounds having the same empirical formulae, i.e., built up of exactly the same constituents, but having different configurations and different properties, are known as *geometrical isomers* (compounds which differ only in the geometrical location of the different components).

Let us now consider the complex ions having a coordination number of 4 (four molecules or ions about the central core). In this case two possibilities present themselves. Let us consider the generalized compound or ion $[A(X)_4]$ where A represents a metallic atom or ion and X the peripheral groups.

The first case to consider is that in which all the X groups lie in a plane, at the corners of a square. This condition is illustrated in Figure 11.3. If two of the X groups are substituted by Y groups, giving the compound or ion $[A(X)_2(Y)_2]$, then if the Y groups are in positions 1 and 2, 2 and 3, 3 and 4, and 1 and 4, they are equivalent. But if the Y groups are in positions 1 and 3 or in 2 and 4, the compound is different from that formed when the Y groups are in the positions previously cited. Again, geometrical isomers are formed. An example of such geometric isomers is found in the compound $[Pt(NH_3)_2Cl_2]Cl_2$.

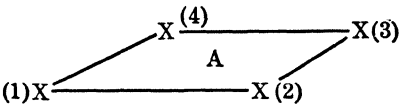


FIG. 11.3 Planar structure of complex ions with coordination number of four.

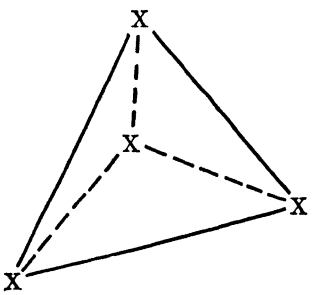


FIG. 11.4 Tetrahedral structure of complex ions with coordination number of four.

The other case to consider is that in which the peripheral groups are located at the corners of a tetrahedron as illustrated in Figure 11.4. In this case, if two Y groups are substituted for two of the X groups, all configurations are alike and no geometrical isomers are formed. This is one criterion in determining the geometrical shapes of the complex ions with coordination number of four.

Only if all four outer groups in the tetrahedral configuration are different can isomers be formed. This condition is illustrated in Figure 11.5. Configuration I cannot be twisted around in any way to be the same as II. This type of isomerism is treated very fully in the study of organic chemistry.

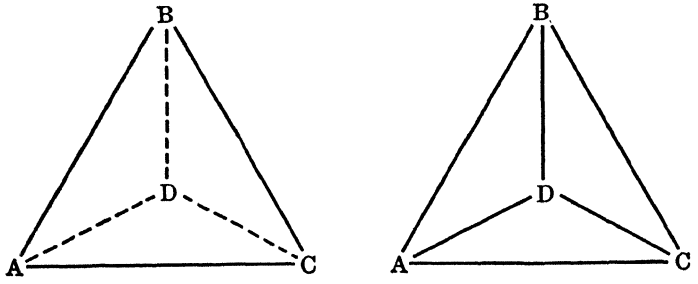


FIG. 11.5 The two kinds of isomers formed when all four groups in a tetrahedral structure are different.

The Electronic Structures of Complex Ions — General Concept. Although the theory of auxiliary valence from the standpoint of electronic structure is not as clear-cut as the simple valence theory heretofore discussed, yet several important correlations present themselves.

Let us consider the structure of the zinc ammonia complex ion, $Zn(NH_3)_4^{++}$, as a basis for our discussion. The *K*, *L*, and *M* shells of the Zn^{++} ion contain 2, 8, and 18 electrons, respectively. Let us assume that each of the four ammonia molecules shares 2 electrons with the central Zn^{++} ion. The zinc-ammonia complex ion structure would then be that illustrated in Figure 11.6. The configuration of electrons about the zinc nucleus in the complex ion would be: 2, 8, 18, and 8, the same structure as that of krypton.

Although it is difficult to find many complex ions the structures of which fall into as clear a picture as this, a rather large number exist for which the total outside electrons contributed as a sharing process by both the central ion and the complementary groups, equals 26 (18 + 8). All the complexes of the Co^{+++} ion fit this scheme. As an example consider the

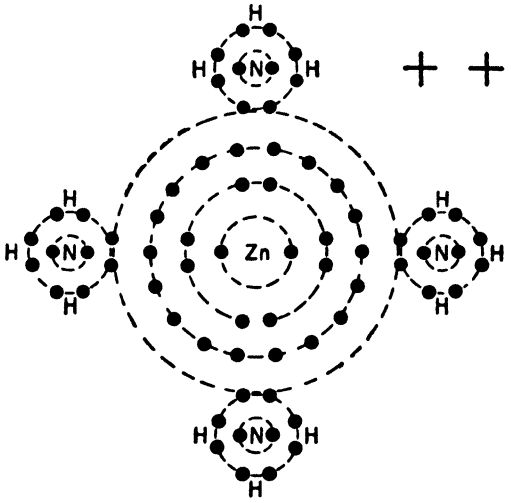


FIG. 11.6 Zinc-ammonia complex ion.

$Co(NH_3)_6^{+++}$ complex ion. The outermost shell of the Co^{+++} ion contains 14 electrons (see table, p. 82) and the six NH_3 groups contribute 12 electrons. The same is true for the $Co(NH_3)_5Cl^{++}$ ion and the $Co(NO_2)_6^{---}$ ion. Some of the other ions and molecules which fall into this category are the platinum ion complexes previously listed, $Fe(CN)_6^{---}$, $CdCl_4^{--}$, $HgBr_4^{--}$, and $Ni(CO)_4$. Many other examples of this kind can be found. The assumption usually made in these cases is that when the electrons assume the 18- and 8-electron outer structure there is little distinction between the electrons in the 18 and the 8 groups.

There are many cases also known for complex ions having less than 26 electrons in the outer shells. The $Cu(NH_3)_4^{++}$ ion, for example, has only 25. Apparently, the 18 shell need not be completely filled to obtain a stable structure. Very seldom, however, do complex ions display more than 26 electrons in the outer two shells. Complexes of the cobaltous ion, Co^{++}, such as $Co(CN)_6^{----}$, are examples of the latter type, but these complex ions are very good reducing agents, i.e., they have a strong tendency to lose this extra electron.

Orbitals and Configurations of Complex Structures. The foregoing general considerations give us a rough picture of complex ion formation through the tendency of the inner metallic ion to form a rare gas structure by the addition of extra electrons contributed by the peripheral groups. In the last few years a great deal of attention has been paid to the more detailed structure of these ions in terms of their orbitals. All the answers are not yet complete. Yet we present these considerations, not because they explain all the facts unequivocally but rather as a point of view which is gaining more and more importance and one with which the student, teacher, and professional chemist will be concerned if he is to keep abreast of the development of structural chemistry. Obviously, in a course such as this, only the viewpoint and the feeling for the subject can be presented. The student should not expect his instructor to explain what may seem to him anomalies. In many cases, nobody knows the answers, as yet.

Let us reconsider the electronic structure of $Zn(NH_3)_4^{++}$ in terms of the orbitals involved. To do this, we refer to Figure 11.7. Here we present the many electrons of the zinc atom, the zinc ion, and the zinc ammonia complex core in terms of the energies of the electron orbitals. The energies of the various orbitals are plotted as ordinates (up and down positions). The lowest orbital (1*s*) is the most stable, i.e., electrons in this orbital require the greatest energy to knock them out, or remove them, by any means, from the atom. The higher up the orbitals are in the figure, the more easily the corresponding electrons are removed. The nearer the lines, representing the various energy states, are to each other, the more alike are the energies of these two states. Electrons can be promoted from a lower to a higher level only if external energy is applied. Such energy is often provided by the bonding of the peripheral groups.

There is also a correlation between the ordinates (the up and down positions) of the orbitals and their distance from the nucleus. The lowest orbitals in the charts are the nearest to the nucleus.

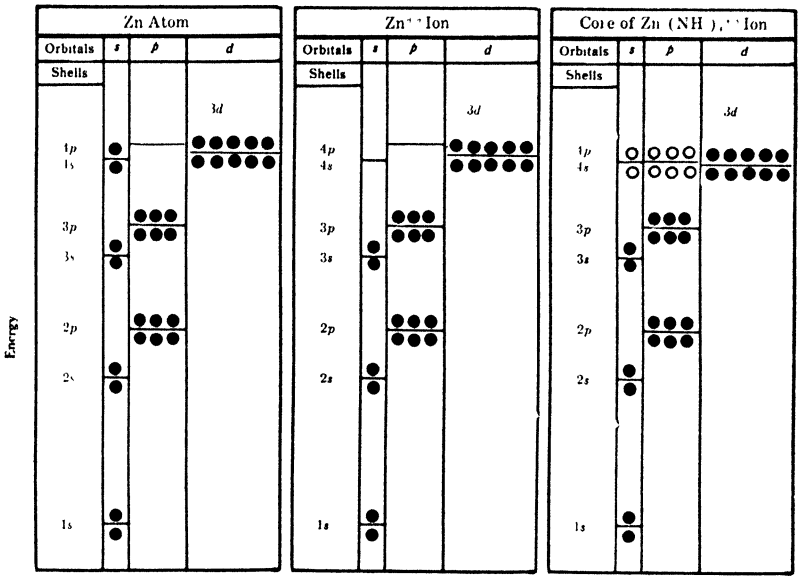


FIG. 11.7 The electronic orbitals of the zinc atom, the Zn^{++} ion, and the core of the $Zn(NH_3)_4^{++}$ ion. The open circles indicate both the bonding electrons and the number of electrons contributed by the peripheral groups.

The numbers associated with the levels represent the principal quantum numbers; thus for the 3*s* orbital the principal quantum number $n = 3$. Note that the only difference between the electronic energy structures of the Zn atom and the Zn^{++} ion is that, in the structure of the Zn^{++} ion, the two 4*s* electrons (the valence electrons) are missing. In the case of $Zn(NH_3)_4^{++}$ ion eight extra electrons are added by the NH_3 molecules (see structure of NH_3 on p. 54). These added electrons are indicated by open circles and act as the covalent bonding electrons holding the NH_3 molecules to the Zn^{++} ion. Before joining the complex these electrons (on the NH_3 molecule) were 2*s* electrons, but in this combination they have lost that identity, i.e., they have changed their character. Note that only *s* and *p* electrons are involved in the bond. The *s* electrons have become identical with the *p* electrons and are said to be promoted; their energies are the same. Four pairs of electrons which are of the *s* and *p* type (promoted) give

rise to a tetrahedral structure (see p. 258 on carbon atom). The 3*d* electrons do not take part in the bonding. In fact, the tetrahedral structure involving only *s* and *p* electrons is the invariable rule, when the *d* shell is filled as in the case of Zn^{++} ion and also Hg^{++}, and when the coordination number is 4.

When the *d* shell is involved in a *d*, *s*, *p* coupling, and when the coordination number is 4, the resultant structure is planar;

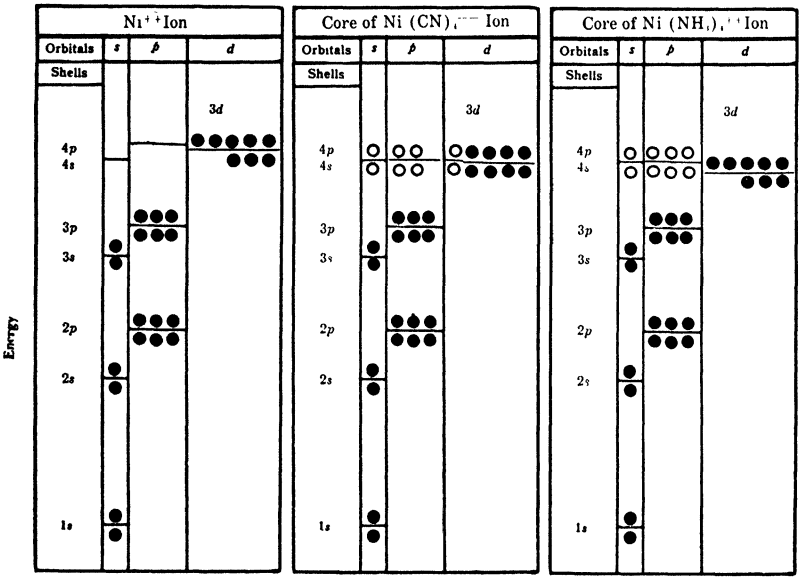


FIG. 11.8 The electronic orbitals of Ni^{++} ion, the core of the $Ni(NH_3)_4^{++}$ ion, and the core of the $Ni(CN)_4^{--}$ ion. The open circles indicate both the bonding electrons and the number of electrons contributed by the peripheral groups.

in the form of a square. To illustrate this, let us consider the ions $Ni(NH_3)_4^{++}$ and $Ni(CN)_4^{--}$. The electronic energy structures for these ions, together with that for the Ni^{++} ion is given in Figure 11.8. Note that in the Ni^{++} ion there are only eight 3*d* electrons two of which are unpaired (according to the rule given on p. 81). These unpaired electrons, which line up magnetically, should give rise to a magnetic moment, i.e., the Ni^{++} should be attracted into a magnetic field (as is a bar magnet). Quantitative magnetic measurements indicate

that there are two unpaired electrons in the Ni^{++} ion, as indicated in Figure 11.8. Only *s* and *p* electrons are involved in the $Ni(NH_3)_4^{++}$ complex ion. This electronic structure is assigned to the ion both because X-ray diffraction analysis indicates that the molecule is tetrahedral (like the carbon atom) and magnetic measurements indicate that there are two free electrons, as in the Ni^{++} ion. The bond type here is sp^3.

On the other hand, $Ni(CN)_4^{--}$ has a structure involving *d*, *s*, and *p* bonding electrons. In this case the bond type is dsp^2. This configuration, according to calculation, indicates a square structure. This is confirmed by X-ray analysis. As would be expected from the structure indicated in Figure 11.8, magnetic measurements indicate that there are no free electrons in the $Ni(CN)_4^{--}$ ion.

In analyzing these diagrams, the student should realize that when electrons are contributed to the central atom by the peripheral groups these electrons lose their identity. They are not labeled. The two electrons which are added to the Ni^{++} ion by the NH_3 molecules to fill in the 3*d* level (or shell) are not necessarily the bonding electrons. The bonding electrons (those indicated by circles) are determined after the structure is completed. The energy or quantum number assignment of any electron does not depend upon its past history.

Let us now consider an example which illustrates the limitations of our knowledge in this subject. For this we shall consider the $Cu(NH_3)_4^{++}$ ion. In Figure 11.9 we give the electronic energy structures of the Cu atom, the Cu^{++} ion, and the core of the $Cu(NH_3)_4^{++}$ complex ion. Looking at the structure of the Cu^{++} ion we might expect that the eight electrons contributed by the NH_3 groups would fall in the 4*s* and 4*p* orbitals and that these orbitals would be responsible for the bonding. If this were so, and if our original postulates were correct, we should expect that the $Cu(NH_3)_4^{++}$ would be tetrahedral in structure. However, X-ray analysis indicates that the structure is a square one. Again, if our original postulate is correct, namely, that a square structure involves, *s*, *p*, and

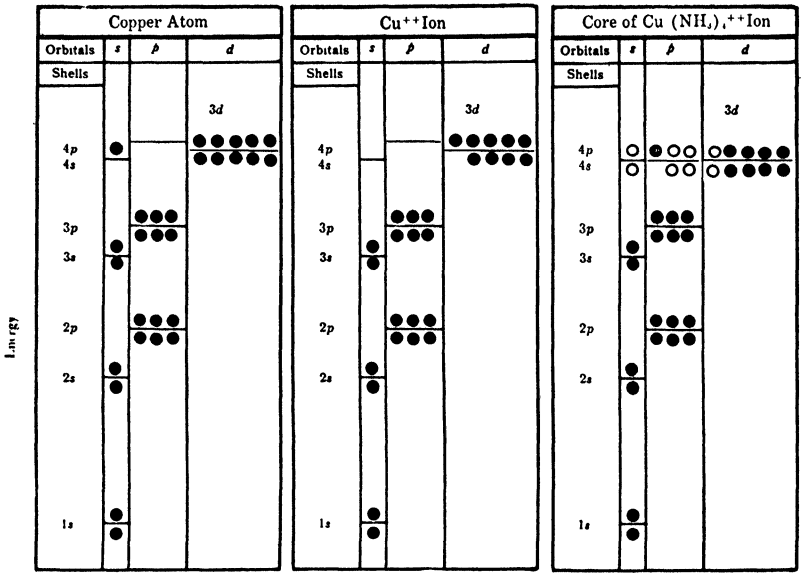


FIG. 11.9 The electronic orbitals of the copper atom, the Cu^{++} ion, and the core of the $Cu(NH_3)_4^{++}$ ion. The open circles indicate both the bonding electrons and the number of electrons contributed by the peripheral groups.

d electrons, we are forced to the structure indicated in the diagram. In this structure the one odd electron is left in the 4*p* level. Magnetic measurement gives us no information, inasmuch as these measurements give only the number of unpaired electrons and no information as to whether any one is in the *d* or *p* level.

The structure of the $Co(NH_3)_6^{+++}$ ion is a regular one. In Figure 11.10 the electronic energy structures for the Co atom, the Co^{+++} ion, and the core of the $Co(NH_3)_6^{+++}$ are given. In forming the Co^{+++} ion the Co atom loses its two 4*s* electrons and one *d* electron, leaving four unpaired *d* electrons. The addition of six ammonia molecules to the complex adds twelve electrons; four in the 3*d*, two in the 4*s*, and six in the 4*p* shell. Twelve valence electrons are necessary, and we might guess that these valence electrons would be those indicated in Figure 11.10. The structure is octahedral, and there are no unpaired electrons. The facts presented here corre-

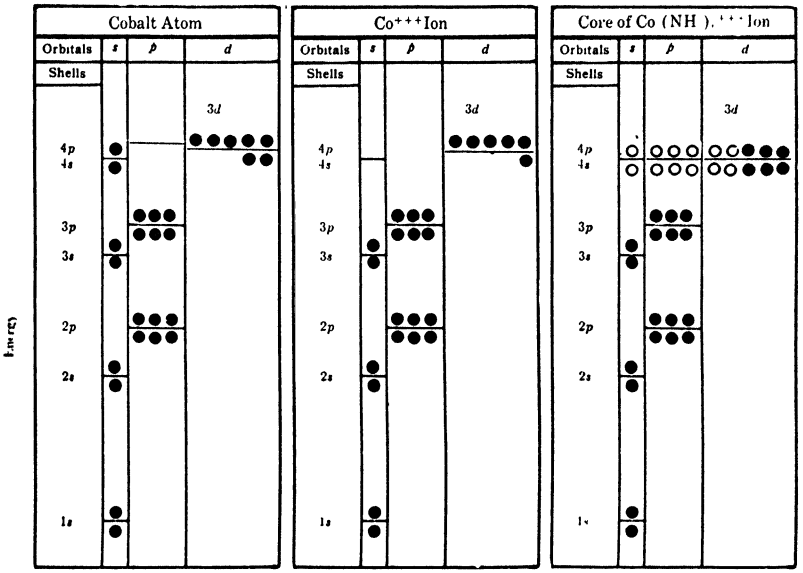


FIG. 11.10 The electronic orbitals of the cobalt atom, the Co^{+++} ion, and the core of the $Co(NH_3)_6^{+++}$ ion. The open circles indicate both the bonding electrons and the number of electrons contributed by the peripheral groups.

spond with the structures determined by X-ray analysis and magnetic measurements. Similar measurements indicate that all complex ions with coordination number six have octahedral structures and are bonded by d^2sp^3 orbitals (here the superscripts indicate the numbers of pairs of electrons). $Fe(CN)_6^{----}$ and $Fe(CN)_6^{---}$ are well known examples. The arguments given here also apply to other elements with similar outer-electron structure, such as Pt, Au, and Hg.

These examples illustrate the state of the science of complex ions. In most cases, with the exception of the $A(X_6)$ complexes which are always octahedral, we cannot predict offhand the geometric structure of these ions. In many cases the geometric structure can be predicted if we know the magnetic data concerning the number of unpaired electrons. At the present state of our knowledge in this field we are able to rationalize the facts quite well, but we cannot predict from general knowledge with any certainty what the geometric

structure of any given ion is. At the present time we are in the hypothesis stage. We guess, we rationalize, we draw analogies, and we coordinate all the known experimental facts which bear upon the problem.

When we can lay down some principle which allows us to predict these structures from very fundamental considerations we shall have a "law" — then the problem will be in hand. A study of the theory of complex ions is a living example of the growth of a scientific theory.

Homoatomic Anions. Many complex anions are known which are formed by the combination of negative ions with neutral atoms or molecules. When the neutral atom or molecule and the negative ion of such a complex involve only a single element, then the complex anion is known as a ***homoatomic*** anion. Potassium iodide is a salt which in water solution ionizes completely to give potassium and iodide ions. Although iodine displays a very low solubility in pure water, when added to an aqueous solution of potassium iodide it dissolves readily. Properties of the solution, such as the lowering of the freezing point and the conductivity, indicate the presence of only two ions. This and other evidence points to the conclusion that a tri-iodide ion is formed through the reaction,

$$I^- + I_2 = I_3^- \qquad (12)$$

The combining weights are also in agreement with this equation. Thus it appears that the negative iodide ion takes up a molecule of iodine, I_2, to form a complex anion, the type which has already been designated as a homoatomic anion. Although this reaction proceeds only as far as the tri-iodide stage in water solution, in the solid condition iodide ions of greater complexity are easily produced. Thus, the iodide ion under suitable conditions will take up molecules of iodine to form complex anions, I_5^-, I_7^-, and I_9^-. As might be expected, an odd number of iodine atoms is always present in the complex anion. Ions having an even number of iodine atoms are not known.

Many other negative ions show properties conforming to

those of the iodide ion, one of which we shall consider in relation to analytical procedures and problems of analysis, namely, the sulfide ion, S^{--}. This ion in water solution reacts with sulfur to produce complex anions which contain only sulfur atoms and bear a charge of -2; the first stage of the reaction is represented by the equation,

$$S^{--} + S = S_2^{--} \tag{13}$$

Evidence points to further reaction to form S_3^{--}, S_4^{--}, S_5^{--} ions, and perhaps anions containing a larger number of sulfur atoms. It will be observed that each ion carries a charge of -2, regardless of the number of sulfur atoms it contains.

In the separation of arsenic from the copper group, yellow ammonium sulfide may be used, since this reagent dissolves the sulfides of the arsenic group but not those of the copper group. The exact composition of the ammonium polysulfide is not known; the solution undoubtedly consists of a mixture of several of the complex sulfide ions mentioned before. For simplicity we shall regard it as containing chiefly S_2^{--} ions. Taking arsenous sulfide as typical of the arsenic group, we may illustrate the action of the ammonium polysulfide (yellow ammonium sulfide) by the equation,

$$As_2S_3(\text{solid}) + 3S_2^{--} = 2AsS_4^{---} + S \tag{14}$$

The arsenous sulfide is oxidized by the polysulfide solution to the thioarsenate ion, AsS_4^{---}. The sulfur formed in reaction (14) is again dissolved by the sulfide solution. Ammonium or sodium sulfide will dissolve As_2S_5 readily but will not dissolve As_2S_3 to any appreciable extent. We may regard the process of solution of As_2S_3 by the polysulfide as one of oxidation by the dissolved sulfur with subsequent solution of the As_2S_5, as illustrated by the equations,

$$As_2S_3 + 2S(\text{dissolved}) = As_2S_5 \tag{15}$$

$$As_2S_5 + 3S^{--} = 2AsS_4^{---} \tag{16}$$

The role played by complex anions and cations in procedures of qualitative analysis will be described in Part II of this text,

when we consider the properties of individual ions, the properties of analytical groups and the methods used for their separation.

Equilibria Involving Complex Ions. When ammonium hydroxide is slowly added to a solution of silver nitrate, there is first observed a brown precipitate of silver hydroxide (or silver oxide). In the presence of a large number of silver ions, there are sufficient hydroxide ions from the ionization of the ammonium hydroxide to exceed the solubility product constant of silver hydroxide. However, the continued addition of ammonium hydroxide to this same solution is found to dissolve the silver hydroxide with the formation of the complex silver ion.

Experiments show that the ammonia molecule is responsible for the dissolving of the silver hydroxide. The original solution of silver nitrate contains only silver and nitrate ions, while the ammonium hydroxide solution introduces four new constituents, ammonium ions, hydroxide ions, free ammonia, and ammonium hydroxide molecules, all of which are in equilibrium with each other:

$$NH_3 + H_2O = NH_4OH = NH_4^+ + OH^- \qquad (17)$$

Neither the ammonium ion nor the hydroxide ion is responsible for the dissolving of silver hydroxide by an excess of ammonium hydroxide. The only two constituents left are free ammonia and ammonium hydroxide molecules. We are not able to distinguish between the two, the equilibrium between them never having been determined with any degree of certainty. We may consider ammonia in water as consisting entirely of free ammonia, NH_3, or of ammonium hydroxide, NH_4OH, molecules, whichever is more convenient. For our purposes it matters little which we choose. The silver-ammonia complex ion, $Ag(NH_3)_2^+$, is the substance formed. (It is to be noted that the names of these complexes are ***ammonia*** complexes and not ***ammonium*** complexes. Ammonia refers to the molecule NH_3; ammonium to the radical NH_4.) The coordination number of the silver ion in

the silver-ammonia complex is 2. The original experiment may now be expressed in the form of two equations,

$$Ag^+ + NH_4OH = AgOH(solid) + NH_4^+ \quad (18)$$

$$AgOH(solid) + 2NH_3 = Ag(NH_3)_2^+ + OH^- \quad (19)$$

Since silver ion and ammonia combine to form the silver-ammonia ion, we would also expect this ion to dissociate somewhat into its constituents,

$$Ag(NH_3)_2^+ = Ag^+ + 2NH_3 \quad (20)$$

The dissociation process is in a general way like the dissociation of weak acids and bases. Lacking sufficient information, the dissociation is expressed by the over-all reaction (equation 20), rather than by steps. According to the equation three kinds of particles are in equilibrium with each other, the silver-ammonia complex ion, silver ion, and ammonia molecules. If an additional amount of silver ions was added to this system, the equilibrium would shift to the left, with the formation of more silver-ammonia ions. The addition of ammonia molecules would have the same effect. Dilution with water would favor the dissociation of the complex to produce more ions. We may write an equilibrium constant for this reaction in the usual way, with the products appearing in the numerator and the reactants in the denominator as follows:

$$\frac{(Ag^+)(NH_3)^2}{(Ag(NH_3)_2^+)} = K = 6 \times 10^{-8} \quad (21)$$

The dissociation constant has a value of 6×10^{-8} which is sufficiently low to signify that the dissociation of the complex ion is slight. What then is the amount of dissociation of this complex ion in a solution in which it is present at moderate concentration?

Let us take, for example, a solution which is 0.1 molar with respect to silver-ammonia and nitrate ions, $Ag(NH_3)_2^+$ and NO_3^-. The concentration of the silver-ammonia ion would be very nearly 0.1 molar provided it were not appreciably dis-

sociated. Since we know from the small value of the equilibrium constant that its dissociation must be very low, we can assume that the concentration of the silver-ammonia ion is practically 0.1 molar at equilibrium. Let X be the number of moles of the complex which dissociate, then the concentration of the silver ion at equilibrium will be X and the concentration of the ammonia molecules, $2X$. Therefore,

$$\frac{(Ag^+)(NH_3)^2}{(Ag(NH_3)_2^+)} = \frac{X(2X)^2}{0.1} = \frac{4X^3}{0.1} = 6 \times 10^{-8}$$

$$4X^3 = 6 \times 10^{-9} \quad \text{and} \quad X^3 = 1.5 \times 10^{-9}$$

$$X = 1.15 \times 10^{-3} \quad \text{and} \quad 2X = 2.3 \times 10^{-3} \text{ mole per liter}$$

In a 0.1 molar solution of the silver-ammonia nitrate, the concentration of the silver ion is then 1.15×10^{-3} mole per liter and the concentration of the free ammonia is twice as great. These values appear to be quite large, larger than one would expect for a highly stable complex. As a matter of fact the silver-ammonia complex is about the least stable of the known ammonia complexes. It will be recalled that in the case of the cobalt-ammonia complexes the addition of sulfuric acid merely converted the original salt to the sulfate and failed to remove readily any ammonia from the complex ion. However, in the case of the silver-ammonia complex the situation is entirely different. When a strong acid is added to a solution of the latter the complex is destroyed due to the combination of the ammonia with hydrogen ion. In this process the equilibrium (equation 20) shifts to the right. Addition of sulfide ion, iodide ion, and other ions which form very insoluble salts with silver ion will also destroy the complex.

But now consider the situation in the presence of the chloride ion. Suppose we attempted to make a solution 0.1 molar with respect to silver-ammonia and chloride ions. What would the concentration of the silver ion be in this solution? It is obvious that the concentration of the silver ion could not be 1.15×10^{-3} mole per liter as it was in the case of the silver-ammonia complex nitrate solution, for with a concentration of

chloride ion in the solution as high as 0.1 mole per liter, the solubility product constant would be exceeded for silver chloride ($K_{SP.} = 2.8 \times 10^{-10}$) by more than one millionfold. Hence, silver chloride would precipitate from solution and the concentration of the silver ion would be greatly reduced. It is apparent that in such a case the silver ion concentration must satisfy both equilibria, the complex ion equilibrium and the solubility product equilibrium of silver chloride. In order to prevent the precipitation of silver chloride in this solution, it is evident that the concentration of the Ag^+ ion must be less than 2.8×10^{-9}, for

$$(Ag^+)(Cl^-) = (Ag^+)(0.1) = 2.8 \times 10^{-10}$$

or

$$(Ag^+) = 2.8 \times 10^{-9}\ M$$

This amount of silver ion must likewise be in equilibrium with the silver-ammonia complex ion, which in turn requires a fairly high concentration of ammonia in solution to prevent the dissociation of the complex ion. In other words, a relatively high concentration of ammonia is required to dissolve silver chloride, the quantitative calculation of which is to be found in the following examples and problems.

Examples of Problems Involving Complex Ions

Example 1.

How many moles of NH_3 must be added to 1 liter of water to enable this solution to dissolve .001 mole of solid silver bromide? The solubility product constant for AgBr has a value of 5×10^{-13}, and the value for the dissociation constant for the silver-ammonia complex ion is 6×10^{-8}.

The reaction which takes place when the solid AgBr dissolves is

$$AgBr_{(s)} + 2NH_3 = Ag(NH_3)_2^+ + Br^- \qquad (1)$$

Two equilibria are involved in this process,

$$AgBr_{(s)} = Ag^+ + Br^- \qquad (2)$$

and

$$Ag(NH_3)_2^+ = Ag^+ + 2NH_3 \qquad (3)$$

The concentration of the Ag^+ ion must be the same for both equilibria as long as solid AgBr and $Ag(NH_3)_2^+$ ion are present. From the equation for the reaction we see that .001 mole of AgBr, when it has just dissolved, produces .001 mole of $Ag(NH_3)_2^+$ ion and .001 mole of Br^- ion. From equation (2) we have

$$(Ag^+)(Br^-) = 5 \times 10^{-13}$$

When (Br^-) becomes .001 M, then

$$(Ag^+) = \frac{5 \times 10^{-13}}{.001} = 5 \times 10^{-10} \text{ mole per liter}$$

This latter value will also be the concentration of the Ag^+ ion which is in equilibrium with the complex ion when the AgBr has just dissolved, since both equilibria are confined to the same solution. Practically all of the silver in the solution is in the form of $Ag(NH_3)_2^+$ ion. Therefore, we may assume that the concentration of the $Ag(NH_3)_2^+$ ion is .001 M. Then, from the equilibrium expression for reaction (3), we have

$$\frac{(Ag^+)(NH_3)^2}{(Ag(NH_3)_2^+)} = \frac{5 \times 10^{-10} \times (NH_3)^2}{.001} = 6 \times 10^{-8}$$

$$(NH_3)^2 = \frac{6 \times 10^{-8} \times 10^{-3}}{5 \times 10^{-10}} = 12 \times 10^{-2}$$

$$(NH_3) = 3.2 \times 10^{-1} = 0.3 \ M \text{ (approximately)}$$

In this calculation the amount of ammonia consumed in forming the complex ion is .002 mole, which is negligible compared with 0.3 mole. However, it should be emphasized that the total amount of ammonia required to dissolve the AgBr is the sum of the combined and free amounts; in other words, it is 0.320 + 0.002 or 0.322 mole. Since the application of the Law of Mass Action is not valid when the solutions become too concentrated, the value of 0.3 M is sufficient, though approximate.

Example 2.

What is the concentration of the Zn^{++} ion in a solution made by adding 0.1 mole of $ZnCl_2$ and 0.4 mole of NH_3 to water to make 1 liter of solution?

Since the formula for the zinc-ammonia complex ion is $Zn(NH_3)_4^{++}$, the amounts of Zn^{++} ion and NH_3 given here are just sufficient to

form 0.1 mole of the complex ion. Let us assume that this amount of the complex ion is formed and that it dissociates until equilibrium is reached, in accordance with the equation

$$Zn(NH_3)_4^{++} = Zn^{++} + 4NH_3$$

The dissociation constant for this complex ion has a value of 3.4×10^{-10}. If X moles of the complex ion dissociate, then, at equilibrium, $(Zn^{++}) = X$, $(NH_3) = 4X$, and $(Zn(NH_3)_4^{++}) = 0.1 - X$. We then have

$$\frac{(Zn^{++})(NH_3)^4}{(Zn(NH_3)_4^{++})} = \frac{X(4X)^4}{0.1 - X} = \frac{(4)^4X^5}{0.1 - X} = \frac{256X^5}{0.1 - X} = 3.4 \times 10^{-10}$$

Neglecting X as compared with 0.1, the expression becomes

$$\frac{256X^5}{0.1} = 3.4 \times 10^{-10}$$

$$X^5 = \frac{3.4 \times 10^{-10} \times 0.1}{2.56 \times 10^2}$$

$$= \frac{3.4 \times 10^{-11}}{2.56 \times 10^2} = 1.33 \times 10^{-13}$$

$$= 133 \times 10^{-15}$$

$$X = 2.7 \times 10^{-3} = .0027 \text{ mole per liter} = (Zn^{++})$$

$$(NH_3) = 4X \cong .01 \text{ mole per liter}$$

The student might encounter some difficulty in finding the fifth root of 133. All that is necessary to do in this case is to obtain the logarithm of 133 which is 2.124. Dividing this by 5 we have 0.425 and the antilog of 0.425 is very nearly 2.7.

Example 3.

(a) How many moles of AgI will dissolve in 1 liter of 1 *M* NH_4OH solution?

Silver iodide is very slightly soluble in pure water ($K_{S.P.} = 8.5 \times 10^{-17}$), but in NH_4OH solution there is some tendency for the Ag^+ ion to combine with the NH_3 to form the $Ag(NH_3)_2^+$ ion, according to the equation

$$AgI_{(s)} + 2NH_3 = Ag(NH_3)_2 + I^- \qquad (1)$$

However, the amount of complex ion formed will be very small since AgI is so insoluble. From the equilibrium expression for the complex ion we have

$$\frac{(Ag^+)(NH_3)^2}{(Ag(NH_3)_2^+)} = 6 \times 10^{-8}$$

Since such a small amount of the complex ion is formed it may be assumed that practically all of the ammonia exists in the free condition in solution and has a value of 1 M. Then

$$(Ag^+) = 6 \times 10^{-8}(Ag(NH_3)_2^+)$$

From this expression it is seen that the concentration of the $Ag(NH_3)_2^+$ ion is very much larger than the concentration of the free Ag^+ ion. This means that practically all of the silver in solution is in the form of the complex ion. Also the concentration of the I^- ion in solution must be practically the same as the concentration of the complex ion.

$$(I^-) = (Ag(NH_3)_2^+)$$

From the solubility product expression, we have

$$(Ag^+)(I^-) = (Ag^+)(Ag(NH_3)_2^+) = 8.5 \times 10^{-17}$$

Substituting in the second expression the value for the $(Ag(NH_3)_2^+)$ above,

$$(Ag^+)\frac{(Ag^+)}{6 \times 10^{-8}} = 8.5 \times 10^{-17}$$

$$(Ag^+)^2 = 8.5 \times 10^{-17} \times 6 \times 10^{-8} = 5 \times 10^{-24}$$

$$(Ag^+) = 2.2 \times 10^{-12}$$

$$(Ag(NH_3)_2^+) = (I^-) = \frac{2.2 \times 10^{-12}}{6 \times 10^{-8}} = 3.7 \times 10^{-5} \text{ mole per liter}$$

Thus the concentration of the I^- ion is 3.7×10^{-5} M; this value is also the solubility of the AgI in the 1 M NH_4OH solution.

The same result could have been obtained in the following manner. Since two equilibria are involved in this system, let us divide one equilibrium expression by the other. Then

$$\frac{(Ag^+)(I^-)}{\frac{(Ag^+)(NH_3)^2}{(Ag(NH_3)_2^+)}} = \frac{(Ag(NH_3)_2^+)(I^-)}{(NH_3)^2} = \frac{8.5 \times 10^{-17}}{6 \times 10^{-8}} = 14 \times 10^{-10}$$

This is the equilibrium constant for reaction (1). But since (NH_3) has a value of 1 M and $(Ag(NH_3)_2^+)$ equals (I^-),

$$(Ag(NH_3)_2^+) \times (I^-) = (I^-)^2 = 14 \times 10^{-10}$$

$$(I^-) = 3.7 \times 10^{-5}\ M = (Ag(NH_3)_2^+)$$

$$= \text{solubility of AgI}$$

(b) What concentration of NH_4OH would be necessary to dissolve .01 M of AgI in 1 liter of solution?

Using the value obtained in (a) we have

$$\frac{(Ag(NH_3)_2^+)(I^-)}{(NH_3)^2} = 14 \times 10^{-10}$$

If .01 mole of AgI were to dissolve, (I^-) and $(Ag(NH_3)_2^+)$ would each have a value of .01 M. Then

$$\frac{(.01)(.01)}{(NH_3)^2} = 14 \times 10^{-10}$$

$$(NH_3)^2 = \frac{1 \times 10^{-4}}{14 \times 10^{-10}} = 7 \times 10^4$$

$$(NH_3) = 2.6 \times 10^2 = 260\ M \text{ (impossible)}$$

This value of 260 M is obtained on the assumption that the Law of Mass Action holds in very concentrated solutions. Evidently, the AgI will not completely dissolve, since it is not possible to obtain at room temperature a solution of ammonia in water of higher concentration than about 18 M.

The method used in (b) could also have been applied in *Example 1*.

Example 4.

A given solution contains .01 mole of Cl^- ion and .07 mole of NH_3 per liter. If .01 mole of solid $AgNO_3$ is added to 1 liter of this solution will AgCl precipitate? The solution of this problem involves two equilibria,

$$AgCl_{(s)} = Ag^+ + Cl^-$$

and

$$Ag(NH_3)_2^+ = Ag^+ + 2NH_3$$

The equilibrium expressions are

$$(Ag^+)(Cl^-) = 2.8 \times 10^{-10}$$

and

$$\frac{(Ag^+)(NH_3)^2}{(Ag(NH_3)_2^+)} = 6 \times 10^{-8}$$

Due to the great stability of the complex ion we shall first assume that .01 mole of this ion is formed from .01 mole of Ag^+ ion. This process would consume .02 mole of NH_3; then .05 mole of NH_3 would be left in solution. Under these conditions, we can calculate the concentration of the free Ag^+ ion in solution.

$$\frac{(Ag^+)(.05)^2}{.01} = 6 \times 10^{-8}$$

$$(Ag^+) = \frac{6 \times 10^{-8} \times .01}{2.5 \times 10^{-3}} = 2.4 \times 10^{-7} \text{ mole per liter}$$

Since .01 mole of Cl^- ion is present per liter of solution, the product of the ion concentrations is $(2.4 \times 10^{-7})(.01)$ or 2.4×10^{-9}. This value is greater than the solubility product constant; therefore, AgCl precipitates.

This problem could be solved in another manner. Let us calculate the amount of Ag^+ ion necessary to start the precipitation of AgCl when .01 *M* Cl^- ion is present. This would be

$$(Ag^+) = \frac{2.8 \times 10^{-10}}{.01} = 2.8 \times 10^{-8}\ M$$

With this amount of free Ag^+ ion in solution and making the assumption that .01 mole of $Ag(NH_3)_2^+$ is formed, we can then calculate the amount of free NH_3 which would be required to maintain these conditions. Then

$$\frac{(2.8 \times 10^{-8})(NH_3)^2}{.01} = 6 \times 10^{-8}$$

$$(NH_3)^2 = \frac{6 \times 10^{-8} \times .01}{2.8 \times 10^{-8}} = 2.1 \times 10^{-2}$$

$$(NH_3) = 1.4 \times 10^{-1} = 0.14\ M.$$

This value for the amount of free ammonia necessary to maintain .01 mole of the complex in solution is much larger than the available ammonia; therefore, AgCl precipitates.

Questions and Problems

1. Is there any definite experimental evidence for the existence of the hydronium ion?
2. Compare the properties of water and ammonia. What is the water analogue of the ammonium ion?
3. What is the ammonia analogue of the hydroxide ion?

4. What are hydrates and ammonates?
5. How does the electronic structure of ions which form complex ions differ from those which do not?
6. On the basis of the coordination theory of Werner, give the structures (not electronic) of the respective complex ions formed when the following salts are dissolved in water: $CoCl_3 \cdot 4NH_3$, $CoCl_3 \cdot 6NH_3$, $Cu(NO_3)_2 \cdot 4NH_3$, $K_3Fe(CN)_6$, and $PtCl_4 \cdot 5NH_3$.
7. Give examples of four complex anions.
8. What is a homoatomic anion? Give two examples.
9. Why does ammonium polysulfide dissolve SnS readily while ammonium sulfide will not?
10. What experiments could be designed to show that the ammonia molecule and not the NH_4^+ nor the OH^- ions is responsible for the solution of silver oxide by excess ammonium hydroxide?
11. If 0.1 mole $AgNO_3$, 0.1 mole NaCl, and 0.2 mole NH_3 were added to 1 liter of water, show by calculation whether AgCl would precipitate.
12. If it were possible to prepare solid $Ag(NH_3)_2Cl$ and if 0.1 mole of this were added to 1 liter of water, would AgCl precipitate? Explain.
13. What is the Zn^{++} concentration in a solution that has been made by adding 0.1 mole $ZnCl_2$ and 1 mole of NH_3 to enough water to give 1 liter of solution?
14. Which gives the greater concentration of Ag^+; a solution made by adding 1 mole $AgNO_3$ and 2 moles KCN to 1 liter of water or a solution made by adding 0.1 mole $AgNO_3$ and 1 mole NH_3? (Note: In the first solution neglect hydrolysis of CN^- ion. In the second solution 0.2 mole NH_3 is used in making $Ag(NH_3)_2^+$. Assume the Law of Mass Action for these more concentrated solutions.)
15. Will 0.1 g. AgBr dissolve in 100 ml. of 1 *M* NH_4OH solution?
16. Will 0.1 g. AgI dissolve in 100 ml. of 1 *M* NH_4OH solution?
17. How much ammonia (expressed in grams) is necessary to dissolve 1 g. AgCl in 100 ml. of water?
18. Calculate the concentration of Ag^+ ion in a solution which is .05 *M* with respect to $Ag(NH_3)_2NO_3$.
19. Calculate the Cu^+ ion concentration in a solution which contains .02 mole $K_3Cu(CN)_4$ per liter.
20. What is the CN^- ion concentration in a solution 0.1 *M* with respect to $K_2Cd(CN)_4$?

21. What is the concentration of NH_3 in a solution which contains .04 mole $Ag(NH_3)_2NO_3$ per liter?
22. (a) Which solution furnishes the higher concentration of Cd^{++} ion, a 0.1 *M* solution of $Cd(NH_3)_4Cl_2$ or a 0.1 *M* solution of $K_2Cd(CN)_4$?
    (b) Give the ratio of the Cd^{++} ion concentrations in these two solutions.
23. If to a liter of a solution, which is .06 *M* with respect to $K_3Cu(CN)_4$ and .06 *M* with respect to $K_2Cd(CN)_4$, CN^- ion is added to increase its concentration to .005 *M*, what will be the concentration of (a) the Cu^+ ion, and (b) the Cd^{++} ion?
24. One liter of a solution contains 0.1 mole of Cl^- ion and 0.1 mole of CN^- ion. To this solution solid silver nitrate is added little by little.
    (a) What happens?
    (b) How many moles of $AgNO_3$ must be added before a precipitate begins to appear?
    (c) When a precipitate first appears, what will be the concentration of the Cl^- ion, of the CN^- ion, and of the Ag^+ ion?
    (Note: AgCN does not precipitate in this solution.)
25. Give the electronic structure for the $CdCl_4^{--}$ ion, as was done for the $Zn(NH_3)_4^{++}$ ion in Figure 11.6.
26. (a) Give the electronic orbital structures for $Fe(CN)_6^{---}$ and $Fe(CN)_6^{----}$ ions as given for $Co(NH_3)_6^{+++}$ ion in Figure 11.10. (These ions have octahedral structures.)
    (b) How many unpaired electrons are there in each of these ions?

CHAPTER
12

Amphoteric Substances

The metals of the alkali and alkaline earth groups of the periodic table are often classified as highly electropositive elements. They exhibit a pronounced tendency to lose electrons and thereby form positive ions. Sodium in its reactions with other elements loses one electron readily to give sodium ion, Na^+, while calcium of the alkaline earth group loses two electrons with the formation of a positive calcium ion, Ca^{++}. These elements are among the first few of the electromotive force (E.M.F.) series of the elements, since this series is one in which the elements are arranged according to the decreasing tendency to lose electrons and form positive ions. In contrast to the alkali metals, sulfur and chlorine of the sixth and seventh groups respectively show a decided tendency to acquire electrons in their reactions with other elements and thereby form negative ions. The latter elements are accordingly termed electronegative; e.g., chlorine can acquire one electron and sulfur two electrons to give ions bearing one and two negative charges, respectively.

Sodium and calcium on the one hand, and sulfur and chlorine on the other, represent extreme types in the classification of the elements according to their tendencies to lose or gain electrons. A large proportion of the elements of the periodic table show dual properties which are characteristic of both sodium and chlorine. They may react with some elements to lose electrons and with other elements to gain them. Hydrogen

under favorable conditions reacts with chlorine to form hydrogen chloride. In this reaction we regard the hydrogen atom as partially giving up an electron to the chlorine atom, and we may regard the hydrogen chloride molecule as one containing hydrogen in the more electropositive condition and chlorine in the more electronegative condition. Likewise, hydrogen reacts directly with lithium to form lithium hydride, LiH. This substance is an excellent conductor of electricity in the fused state in which it must be ionized as positive lithium ions and negative hydrogen or hydride ions, H^-, since upon electrolysis hydrogen is liberated at the anode. In this reaction the hydrogen atom acquires an extra electron to form a negative hydrogen ion. Apparently the hydrogen atom has a greater tendency to acquire an electron and a smaller tendency to lose an electron than has the lithium atom. So far as chemical evidence goes, the lithium atom shows no tendency to form negative ions. Thus, hydrogen may behave in a dual manner, it may gain or lose electrons depending upon its environment. If it is in the presence of a strongly electronegative element such as chlorine it will behave electropositively, while in the presence of a strongly electropositive element, for example lithium, it will behave electronegatively. Such elements lie in an intermediate position in the E.M.F. series and are sometimes spoken of as ***amphoteric*** elements, a designation which implies this dual character.

Many other elements show amphoteric properties in their reactions. Thus, sulfur, selenium, and tellurium of the sixth group of the periodic table react with chlorine and oxygen to form chlorides and oxides. They likewise react with sodium, potassium, and other electropositive elements to form sulfides, selenides, and tellurides which are salts. Examples of such compounds are: Na_2S, Na_2Se, Na_2Te, K_2S, K_2Se, and K_2Te. Phosphorus, arsenic, antimony, and bismuth of the fifth group of the periodic table behave in a similar manner, while germanium, tin, and lead may be mentioned as typical examples of the fourth-group elements. Even elements in the second and third groups such as zinc, cadmium, mercury, gallium, indium,

and thallium will combine with sodium and other strongly electropositive elements to form definite compounds. This dual behavior is the general case rather than the exceptional one.

Amphoteric Hydroxides. Many of the elements which show this dual behavior in the ability to acquire and to lose electrons in their reactions show another, but somewhat different, type of duality in the reactions of their hydroxides. It is well known that the oxides of strongly electropositive elements such as Na_2O, K_2O, CaO, and MgO form strong bases in water solution, NaOH, KOH, $Ca(OH)_2$, and $Mg(OH)_2$, respectively. However, oxides of strongly electronegative elements such as SO_3, N_2O_5, and Cl_2O_7 in water solution are decidedly acidic in character; they are the anhydrides of the acids, H_2SO_4, HNO_3, and $HClO_4$, respectively.

Oxides of most of the elements which lie in an intermediate position in the E.M.F. series of elements, which are neither strongly electropositive nor strongly electronegative, show both acidic and basic properties in water. As would be predicted, such acids and bases are extremely weak. Thus lead oxide, PbO; aluminum oxide, Al_2O_3; chromic oxide, Cr_2O_3; zinc oxide, ZnO; stannous oxide, SnO; and antimonous oxide, Sb_2O_3, are the anhydrides of the very weak hydroxides, $Pb(OH)_2$, $Al(OH)_3$, $Cr(OH)_3$, $Zn(OH)_2$, $Sn(OH)_2$, and $Sb(OH)_3$, respectively, which hydroxides may also be regarded as very weak acids. To emphasize the acidic properties of these hydroxides their formulae could be written H_2PbO_2, H_3AlO_3 (or $HAlO_2 + H_2O$), H_3CrO_3 (or $HCrO_2 + H_2O$), H_2ZnO_2, H_2SnO_2, and H_3SbO_3 (or $HSbO_2 + H_2O$). In the cases of H_3AlO_3, H_3CrO_3, and H_3SbO_3 only one hydrogen is replaceable in water solution, the simpler and more informative formulae $HAlO_2$, $HCrO_2$, and $HSbO_2$, respectively, are usually used. In each of these cases the same substance may be represented by two differently arranged formulae; by convention, one emphasizes the basic properties and the other, the acidic properties.

All of these hydroxides are very slightly soluble in water but dissolve readily when either a strong acid such as hydro-

chloric acid or a strong base such as sodium hydroxide is present. Taking $Al(OH)_3$ as an example, we may write,

$$Al(OH)_3 + 3HCl \text{ (in solution)} = AlCl_3 \text{(in solution)} + 3H_2O \quad (1)$$

and

$$Al(OH)_3 + NaOH \text{ (in solution)} = NaAlO_2 \text{(in solution)} + 2H_2O \quad (2)$$

Both of these reactions appear familiar in that the products in each case are a salt and the solvent, water; in other words, they are neutralization reactions. Since both HCl, an acid, and NaOH, a base, are used, it must necessarily follow that the aluminum hydroxide is functioning in equation (1) as a base and in equation (2) as an acid. Hydroxides which show properties characteristic of both acids and bases are known as ***amphoteric hydroxides.***

The ionization of aluminum hydroxide when acting both as a weak acid and a weak base is expressed in the following equation:

$$Al^{+++} + 3OH^- = \left\{ \begin{matrix} Al(OH)_3 \\ H_3AlO_3 \end{matrix} \right\} \text{(solid)} = AlO_2^- + H^+ + H_2O \quad (3)$$

For lack of definite information regarding the ionization of aluminum hydroxide as a base we have expressed the reaction as one producing $3OH^-$ ions. It is a weak polyacid base and undoubtedly would not be expected to ionize highly even in the first stage, let alone in the two successive stages. However, at present it is not experimentally feasible to determine the exact extent of ionization of aluminum hydroxide for each of the three steps. Equation (3) also shows the aluminate ion, AlO_2^-, a product of the ionization of aluminum hydroxide as an acid.

We may now predict, with the aid of Le Chatelier's Rule, the effect of strong acids and of strong bases upon the equilibrium. If a strong acid, such as hydrochloric acid, is added to a suspension of aluminum hydroxide in water, the hydrogen ions which are in excess combine with some of the hydroxide ions to form water. According to the Rule of Le Chatelier,

we would predict a shift in the equilibrium to the left. The tendency is for the equilibrium to shift in such a way as to attempt to retrieve the loss of hydroxide ions. This can be done only by the further dissociation of aluminum hydroxide from the solid phase. As fast as hydroxide ions are produced by this process, they are removed by hydrogen ions. Finally, all the solid dissolves and the concentration of the hydroxide ions in solution still remains at a very small value due to the continued removal of the hydroxide by hydrogen ions. Although the hydroxide ions are depleted as fast as they are produced by the ionization of the aluminum hydroxide, the latter reaction also yields large amounts of aluminum ions which remain as such in solution. Therefore, when hydrochloric acid is used as a source of hydrogen ions, the final result is that the solid aluminum hydroxide dissolves and the solution contains aluminum and chloride ions. Hydrogen and hydroxide ions will also be present in concentrations which must satisfy the water equilibrium, $(H^+)(OH^-) = 1 \times 10^{-14}$.

The addition of a strong base such as sodium hydroxide furnishes a large concentration of hydroxide ions. According to Le Chatelier's Rule the equilibrium should shift in such a direction as to use up hydroxide ions; that is, it should shift to the right as equation (3) is written. Naturally, hydrogen ions will be removed from the reaction medium by their combination with hydroxide ions to form water. When this happens more aluminum hydroxide will dissolve to give hydrogen ions and aluminate ions in an attempt to retrieve the loss of hydrogen ions. The hydrogen ions are removed as fast as they are produced and finally, when all of the solid aluminum hydroxide has dissolved, sodium ions and aluminate ions will be left in solution in large quantities, and the hydrogen ion and hydroxide ion concentrations will be in accord with that demanded by the water equilibrium.

Aluminum hydroxide has been taken here as a typical example of an amphoteric hydroxide. Others previously mentioned, $Pb(OH)_2$, $Cr(OH)_3$, $Zn(OH)_2$, $Sn(OH)_2$, and $Sb(OH)_3$ behave similarly in that they dissolve and function as bases

in the presence of a strong acid, and also dissolve and function as acids in the presence of a strong base. The latter reaction is the more unfamiliar one and in the presence of sodium hydroxide the following ions are produced: $HPbO_2^-$, CrO_2^-, ZnO_2^{--}, $HSnO_2^-$, and SbO_2^-, namely, biplumbite, chromite, zincate, bistannite, and antimonite ions.

As was previously stated the amphoteric hydroxides are derived from elements occupying an intermediate position in the E.M.F. series. They must necessarily occupy a similar intermediate position in a given series of the periodic table since the elements of the main groups to the left are strongly electropositive, while those of the main groups to the right are strongly electronegative. Those elements which show both properties lie in between these two extremes. As one passes from one extreme position of the table to the other, the change in properties is not an abrupt one; on the contrary, it is very gradual. As an example, let us choose the series of the table beginning with the inert gas argon, atomic number 18 (see back cover); the next element, potassium, forms a very strong base, potassium hydroxide. Under ordinary conditions of temperature it acts only as a base in water solution. Calcium hydroxide, representative of the second group, likewise possesses only basic properties in water. Scandium hydroxide is also a strong base, but titanium hydroxide, vanadium hydroxide, and chromium hydroxide, hydroxides of the fourth, fifth, and sixth groups, respectively, in the series under consideration, show amphoteric properties in that they form titanates, vanadites, and chromites with strong bases. Vanadates and chromates are also known, being derived from the higher valence hydroxides, which, however, are distinctly more acidic than basic in nature. In the seventh group manganous hydroxide, $Mn(OH)_2$, is a moderately strong base and possesses very little acid properties; while H_2MnO_4, manganic acid, is a weak acid and $HMnO_4$, permanganic acid, is a very strong acid. In general, the higher the valence of the metal in any two or more similarly derived acids the more acidic properties it will display. Thus, stannic acid is a stronger

acid than stannous acid, arsenic is stronger than arsenous, chromic stronger than chromous, etc. Ferric, ferrous, cobaltous, nickelous, and cuprous hydroxides are distinctly basic in aqueous solutions and acid properties are almost entirely lacking. The next element of the series, zinc, atomic number 30, forms a hydroxide, $Zn(OH)_2$, which is well known for its amphoteric properties. Following zinc hydroxide are $Ga(OH)_3$, $Ge(OH)_4$, and $AsO(OH)_3$, all of which dissolve in sodium hydroxide solution to produce gallate, germanate, and arsenate ions. H_2SeO_4, selenic acid, and $HBrO_3$, bromic acid, are decidedly acidic in water. Thus, in this series of eighteen elements, many of their hydroxides are amphoteric.

Within a given group, occupying an intermediate position in the periodic table, the amphoteric properties change as one proceeds from the element of lower to one of higher atomic weight. Thus HNO_2 shows only acid properties; H_3PO_3 likewise is acidic; H_3AsO_3 or $As(OH)_3$ and H_3SbO_3 or $Sb(OH)_3$ are amphoteric, while $Bi(OH)_3$ is basic in its reactions. Thus, in passing from nitrogen to bismuth in the main fifth group, the hydroxides change from strong acids to weak acids and moderately strong bases, but the change is a gradual one.

Amphoteric Sulfides. Sulfur occupies a position in the sixth group of the periodic table just below oxygen. Hence, many of the compounds of sulfur contain the sulfur atom in a position similar to that occupied by oxygen in the more familiar oxygen compounds. In qualitative analysis we are particularly interested in the amphoteric nature of analogous sulfides and oxides. Since hydrogen sulfide is the analogue of water, the bisulfide ion of the hydrogen sulfide system corresponds to the hydroxide ion of the water system, as the following equations readily demonstrate:

$$H_2O = H^+ + OH^- \tag{4}$$

$$H_2S = H^+ + SH^- \tag{5}$$

Likewise, the metal sulfides are analogues of the metal oxides; K_2S, CaS, As_2S_5, and Sb_2S_3 in the hydrogen sulfide system correspond to K_2O, CaO, As_2O_5, and Sb_2O_3, respectively, in

the water or oxygen system. On the basis of these analogies, one might expect sulfides to dissolve in the presence of bisulfide ions in the same way that oxides or hydroxides, in an aqueous medium, dissolve in the presence of hydroxide ions. When the sulfides behave in this manner, they are exhibiting acid properties. A few examples will serve to illustrate this type of reaction.

$$As_2S_5 + 6HS^- = 2AsS_4^{---} + 3H_2S \quad (6)$$

or

$$As_2S_5 + 2HS^- = 2AsS_3^- + H_2S \quad (7)$$

$$Sb_2S_5 + 6HS^- = 2SbS_4^{---} + 3H_2S \quad (8)$$

Actually the H_2S produced in the above equations reacts with the OH^- ions to produce HS^- ions and water. Therefore the equation for the process of the solution of As_2S_5 by HS^- ions in alkaline solution is

$$As_2S_5 + 3HS^- + 3OH^- = 2AsS_4^{---} + 3H_2O \quad (9)$$

rather than that given by equation (6). The same would be true for the reactions represented by equations (7) and (8).

Another explanation may be given for the fact that arsenic and antimony sulfides dissolve in alkaline sulfide solution. In such a solution, the concentration of the sulfide ion is certainly appreciable and much larger than the concentration of the oxide ion, O^{--}, in solutions containing alkali hydroxides, since the bisulfide ion is dissociated to a much greater extent to give hydrogen and sulfide ions than is the hydroxide ion to give hydrogen and oxide ions. As a matter of fact, it has not been possible through experiment to determine the concentration of the oxide ion. Due to the presence of sulfide ions in alkaline sulfide solutions, it is possible, however, to explain the solubility of arsenic and antimony sulfides as follows:

$$As_2S_5 + 3S^{--} = 2AsS_4^{---} \quad (10)$$

$$As_2S_3 + 3S^{--} = 2AsS_3^{---} \quad (11)$$

$$As_2S_5 + S^{--} = 2AsS_3^- \quad (12)$$

$$Sb_2S_5 + 3S^{--} = 2SbS_4^{---} \quad (13)$$

Antimony and tin in the lower valence states are much more strongly basic or more weakly acidic than in the higher valence states. Accordingly, antimonous sulfide dissolves with difficulty in ammonium sulfide solution and stannous sulfide is practically insoluble in this medium. However, antimonic and stannic sulfides are readily soluble in this same solvent.

Just as oxygen can oxidize a lower valence oxide to a higher valence one, so sulfur can oxidize a lower to a higher valence sulfide. Ammonium polysulfide is ammonium sulfide containing dissolved sulfur (chemically combined with the sulfide ion). When the lower sulfides are treated with ammonium polysulfide they are oxidized to the higher valence state in which they are readily soluble. This process of solution has already been discussed in the previous chapter, as an illustration of complex ion formation. The process of solution of the amphoteric sulfides may be explained on the basis of the amphoteric properties of the sulfides and on the basis of sulfur in sulfide solution acting as an oxidizing agent.

Application of Amphoteric Substances to Analysis. Suppose we consider a solution which has been obtained as a hydrochloric acid extraction of an ore known to contain iron, zinc, and aluminum. We wish to separate these elements from each other in solution by methods which will reduce the difficulties to a minimum. The solution contains all three elements in the form of their chlorides and is slightly acidic. We might first add sodium hydroxide to the solution to the point of neutralization and obtain a precipitate containing all three substances in the form of hydroxides, $Fe(OH)_3$, $Al(OH)_3$, and $Zn(OH)_2$. Knowing that both zinc and aluminum hydroxides are decidedly amphoteric in nature, let us continue the addition of the sodium hydroxide solution. Both $Al(OH)_3$ and $Zn(OH)_2$ dissolve immediately with the formation of aluminate and zincate ions, respectively; however, ferric hydroxide is not amphoteric and does not dissolve in the presence of excess hydroxide ion. Accordingly, the ferric hydroxide can be separated at this point by filtration. Ammo-

nium hydroxide would not behave in the same way as the sodium hydroxide since the former does not furnish sufficient hydroxide ions to dissolve aluminum hydroxide.

If it should appear desirable to separate the aluminum from the zinc, the filtrate could be treated with hydrochloric acid until the zinc and aluminum hydroxides dissolve, and to this solution could be added excess ammonium hydroxide. Under these conditions the aluminum hydroxide would precipitate and the zinc would stay in solution in the form of the zinc-ammonia ion, $Zn(NH_3)_4^{++}$.

Thus, through the application of the amphoteric properties of the aluminum and zinc hydroxides and the subsequent use of the ability of the zinc ion to form complex ions, it is possible to readily separate these three elements from each other. The hydroxides, $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$ may also be separated from each other by the same general procedure; $Al(OH)_3$ and $Cr(OH)_3$ are amphoteric while $Fe(OH)_3$ is not. Chromium and aluminum may be subsequently separated from each other by the oxidation of the chromite ion, CrO_2^-, to the chromate ion, CrO_4^{--}. Chromium ion combining with other elements displays two principal valences of $+3$ and $+6$, while aluminum has only the one valence of $+3$. Other examples to illustrate the behavior of amphoteric hydroxides and sulfides in the separation and identification of ions are too numerous to mention here. However, several illustrations will be given in Part II of this text relating to the separation of the analytical groups and the properties of individual ions.

Amphoteric Hydroxides as Coordinated Complexes. To illustrate the application of the Brønsted definitions to problems involving amphoteric hydroxides, let us choose aluminum hydroxide as the example for consideration.

Many hydroxides do not have a constant and definite composition. Nevertheless we use definite formulae to designate them. In our previous discussions, for the sake of convenience we designated aluminum hydroxide by the formula $Al(OH)_3$. According to this formula this substance should

consist of 34.58 percent aluminum, 61.55 percent oxygen, and 3.87 percent hydrogen. Under most circumstances an analysis of aluminum hydroxide would not give these percentages but other rather widely different values. The reason for this discrepancy is that aluminum hydroxide when freshly precipitated contains additional water not indicated in the formula, $Al(OH)_3$. This additional water may be chemically bound to the aluminum atom or it may merely be adsorbed. When the aluminum hydroxide is dried it loses water, and upon continued drying the loss of water does not stop when the composition corresponds to the formula $Al(OH)_3$, but rather when its composition is such as to correspond more nearly to the formula AlO(OH) or $Al_2O_3 \cdot H_2O$. Upon excessive drying (by heating) all the water is lost and only the oxide Al_2O_3 remains. The formula for aluminum hydroxide is therefore often written as $Al_2O_3 \cdot XH_2O$. But for convenience, most chemists have adopted the formula $Al(OH)_3$ for this substance.

To explain the hydrolysis of the aluminum ion by the Brønsted definitions we may write its formula as $Al(H_2O)_6^{+++}$, assuming a coordination number of six for the aluminum ion. In keeping with this same concept we can also write an analogous formula for aluminum hydroxide in the hydrated form, again using the coordination number of six. Its formula would then be $Al(H_2O)_3(OH)_3$. Using this formula let us explain the amphoteric nature of aluminum hydroxide as we have done with the older definitions. As an amphoteric hydroxide this substance is both a proton donor and a proton acceptor. When dissolved in water it may be regarded as accepting protons from and donating them to water molecules.

$$\underset{\text{Acid}_1}{Al(H_2O)_3(OH)_{3(s)}} + \underset{\text{Base}_2}{H_2O} = \underset{\text{Base}_1}{Al(H_2O)_2(OH)_4^-} + \underset{\text{Acid}_2}{H_3O^+} \qquad (14)$$

$$\underset{\text{Base}_2}{3H_2O} + \underset{\text{Acid}_1}{Al(H_2O)_6^{+++}} = \underset{\text{Acid}_2}{3H_3O^+} + \underset{\text{Base}_1}{Al(H_2O)_3(OH)_{3(s)}} \qquad (15)$$

In the first equilibrium (14) aluminum hydroxide is represented as a weak acid, i.e., as a proton donor. In equation (15) reading right to left, it is represented as a proton ac-

ceptor or as a base. This latter process could be expressed in three stages, i.e., aluminum hydroxide is a tri-acid base, but for convenience we have combined all three steps in this single equation. Both reactions (14) and (15) are acid-base reactions. If aluminum hydroxide is treated with a strong acid the equilibrium (15) is shifted to the left; the solid is dissolved and the aluminum ion, $Al(H_2O)_6^{+++}$ is formed. If a sodium hydroxide solution is added to a suspension of aluminum hydroxide, the OH^- ion of the solution combines with the H_3O^+ ion, shifting the equilibrium reaction (14) to the right, and aluminate ion $Al(H_2O)_2(OH)_4^-$ is formed. The over-all reaction for this latter process is

$$Al(H_2O)_3(OH)_{3(s)} + OH^- = Al(H_2O)_2(OH)_4^- + H_2O \quad (16)$$

The amphoteric nature of zinc hydroxide can be explained in an analogous way. In this case the formula of zinc hydroxide can be written as $Zn(H_2O)_2(OH)_2$; the coordination number of zinc is assumed to be four. Then the equilibrium reactions representing the amphoteric nature of zinc hydroxide are

$$\underset{\text{Acid}_1}{Zn(H_2O)_2(OH)_{2(s)}} + \underset{\text{Base}_2}{2H_2O} = \underset{\text{Base}_1}{Zn(OH)_4^{--}} + \underset{\text{Acid}_2}{2H_3O^+} \quad (17)$$

$$\underset{\text{Acid}_1}{Zn(H_2O)_4^{++}} + \underset{\text{Base}_2}{2H_2O} = \underset{\text{Acid}_2}{2H_3O^+} + \underset{\text{Base}_1}{Zn(H_2O)_2(OH)_{2(s)}} \quad (18)$$

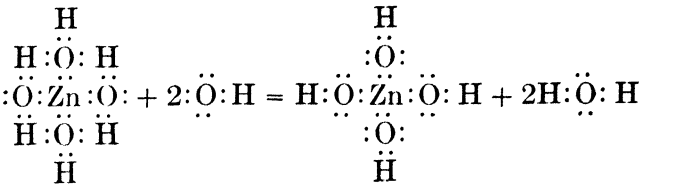
In acid solution the equilibrium of the lower equation is shifted to the left; $Zn(H_2O)_2(OH)_{2(s)}$ dissolves and $Zn(H_2O)_4^{++}$ is formed. In alkaline solution the OH^- ion combines with the H_3O^+ ion and the equilibrium of reaction (17) is shifted to the right. The over-all reaction for the dissolving of solid zinc hydroxide by a solution of sodium hydroxide is then

$$Zn(H_2O)_2(OH)_{2(s)} + 2OH^- = Zn(OH)_4^{--} + 2H_2O \quad (19)$$

All amphoteric hydroxides may be treated in the same way. In each case the accepted coordination number of the metal ion should be used.

The structural form of zinc hydroxide in solution is similar to that given for zinc ammonia complex (see Fig. 11.6) except

that two of the NH_3 groups are replaced by OH^- ions and two by water molecules. Structurally, equation (19) may be represented by the equation



(20)

In this reaction each of the two water molecules in the complex may be thought of as losing a hydrogen ion, which combines with the OH^- ion to produce water. As a result $Zn(OH)_4]^{--}$ complex ion is formed. The latter ion is essentially hydrated zincate ion.

Examples of Problems Involving Amphoteric Substances

Example 1.

How many moles of NaOH must be added to 1 liter of water to dissolve completely .001 mole of zinc hydroxide?

The reaction is expressed by the equation

$$Zn(OH)_{2(s)} + 2OH^- = ZnO_2^{--} + 2H_2O$$

Zinc hydroxide is a weak acid and ionizes to give H^+ and ZnO_2^{--} ions.

$$Zn(OH)_{2(s)} = ZnO_2^{--} + 2H^+$$

The equilibrium expression for the ionization of $Zn(OH)_2$ as an acid is

$$(ZnO_2^{--})(H^+)^2 = 1 \times 10^{-29}$$

If .001 mole of $Zn(OH)_2$ dissolves, then .001 mole of ZnO_2^{--} ion will be produced.

$$(ZnO_2^{--})(H^+)^2 = (.001)(H^+)^2 = 1 \times 10^{-29}$$
$$(H^+)^2 = 1 \times 10^{-26}$$
$$(H^+) = 1 \times 10^{-13} \text{ mole per liter}$$

From the water equilibrium (OH^-) may be calculated.

$$(OH^-) = \frac{1 \times 10^{-14}}{(H^+)} = \frac{1 \times 10^{-14}}{1 \times 10^{-13}} = 0.1 \text{ mole per liter}$$

This value for (OH^-) is the amount in solution at equilibrium after the .001 mole of $Zn(OH)_2$ has dissolved. But to dissolve the $Zn(OH)_2$ an additional amount (.002 mole) of OH^- ion was required. Therefore the total amount of OH^- ion needed to dissolve .001 mole of $Zn(OH)_2$ and to maintain it in solution as ZnO_2^{--} ion is 0.1 + .002 or 0.102 mole.

(The constant used in this calculation is not accurate enough nor is the Law of Mass Action sufficiently valid to warrant taking into account the amount of OH^- ion consumed in the reaction. Therefore the answer 0.1 mole, instead of 0.102 mole, is more appropriate.)

Example 2.

A solution is .05 *M* with respect to OH^- ion and is in equilibrium with solid $Pb(OH)_2$. What is the concentration of (a) the Pb^{++} ion, (b) the $HPbO_2^-$ ion, and (c) the H^+ ion in the solution? (Disregard the second step of ionization of $Pb(OH)_2$ as an acid.)

In this solution the following equilibria are present.

$$Pb(OH)_{2(s)} = Pb^{++} + 2OH^- \qquad (1)$$

$$Pb(OH)_{2(s)} = HPbO_2^- + H^+ \qquad (2)$$

Since (OH^-) has a value of .05 *M* and the value for the solubility product constant for $Pb(OH)_2$ is 4×10^{-15}, we have from equation (1)

$$(Pb^{++})(OH^-)^2 = (Pb^{++})(.05)^2 = 4 \times 10^{-15}$$

Therefore

$$(Pb^{++}) = \frac{4 \times 10^{-15}}{2.5 \times 10^{-3}} = 1.6 \times 10^{-12}\ M$$

From equation (2) we may write

$$(HPbO_2^-)(H^+) = 2 \times 10^{-16}$$

Since the value for (OH^-) is .05 *M*, (H^+) must be

$$\frac{1 \times 10^{-14}}{(OH^-)} = \frac{1 \times 10^{-14}}{5 \times 10^{-2}} = 2 \times 10^{-13}\ M$$

Then

$$(HPbO_2^-)(2 \times 10^{-13}) = 2 \times 10^{-16}$$

$$(HPbO_2^-) = \frac{2 \times 10^{-16}}{2 \times 10^{-13}} = 1 \times 10^{-3}\ M$$

Example 3.

How many moles of $Cr(OH)_3$ will dissolve in 1 liter of 0.2 *M* NaOH solution? The equation for the reaction is

$$Cr(OH)_{3(s)} + OH^- = CrO_2^- + 2H_2O$$

According to this equation the number of moles of $Cr(OH)_3$ which dissolves will be equivalent to the number of moles of CrO_2^- ion in solution.

As an acid $Cr(OH)_3$ ionizes as follows:

$$Cr(OH)_{3(s)} = CrO_2^- + H^+ + H_2O$$

The ionization constant has a value of 1×10^{-16}; therefore

$$(CrO_2^-)(H^+) = 1 \times 10^{-16}$$

Since (OH^-) has a value of 0.2 *M*, (H^+) is $\frac{1 \times 10^{-14}}{0.2}$ or 5×10^{-14} *M*.

Then

$$(CrO_2^-)(5 \times 10^{-14}) = 1 \times 10^{-16}$$

$$(CrO_2^-) = \frac{1 \times 10^{-16}}{5 \times 10^{-14}} = 2 \times 10^{-3} \text{ mole per liter}$$

Therefore .002 mole of $Cr(OH)_3$ dissolves in 1 liter of 0.2 *M* NaOH solution.

Questions and Problems

1. What are the anhydrides of the following substances: (a) HNO_3, (b) $Ca(OH)_2$, (c) NaOH, (d) H_2SO_4, (e) $Mg(OH)_2$, and (f) $HClO_4$?
2. Give the formulae of the hydroxides of which the following are the anhydrides: ZnO, Cr_2O_3, PbO, Al_2O_3, and Sb_2O_3.
3. Rearrange the formulae of the hydroxides given in question 2 in such a way as to emphasize their acidic properties.
4. Write the equations for the equilibrium involved when aluminum hydroxide acts both as an acid and as a base.
5. How may the equilibrium in problem (4) be shifted so as to produce (a) a large concentration of Al^{+++} ions, (b) a large concentration of AlO_2^- ions?
6. Are the elements in the first main group of the periodic system more electronegative than those of the fourth group or vice versa?

7. In the series of 18 elements of the periodic table beginning with argon, name those the hydroxides of which are not amphoteric.
8. Which hydroxide acts as a stronger acid, $Sn(OH)_2$ or $Sn(OH)_4$?
9. Predict which hydroxide would act as the stronger acid, $Ge(OH)_2$ or $Ge(OH)_4$. Explain the basis of your prediction.
10. Write the formula for the sulfur analogue of each one of the following oxygen compounds: (a) H_2O, (b) SnO, (c) K_2O, (d) CO_2, (e) OH^-.
11. Give equations for the reactions involved when As_2O_5 is dissolved by a solution containing OH^- and when As_2S_5 is dissolved by a solution containing HS^- ions.
12. Why will SnS dissolve readily in ammonium polysulfide while in ammonium sulfide it is soluble only to a very small extent?
13. Making use of the amphoterism of $Zn(OH)_2$ and $Al(OH)_3$ and the complex-forming properties of Zn^{++} show how $Zn(OH)_2$, $Al(OH)_3$, and $Fe(OH)_3$ may be separated from each other.
14. How many moles of NaOH must be added to 100 ml. of water to dissolve completely .001 mole of $Zn(OH)_2$?
15. A saturated solution of $Zn(OH)_2$ in water contains the following ions in equilibrium with each other: Zn^{++}, ZnO_2^{--}, H^+, and OH^-. Calculate the concentration of each ion in such a solution. (Note: from the solubility product constant for $Zn(OH)_2$ calculate (Zn^{++}) and (OH^-), then obtain (H^+) from the water equilibrium, and finally calculate (ZnO_2^{--}) from the equilibrium for the ionization of $Zn(OH)_2$ as an acid.)
16. What is the concentration of the Zn^{++} ion and of the ZnO_2^{--} ion in a solution which is .01 molar with respect to OH^- ion and which is in equilibrium with solid $Zn(OH)_2$?
17. A solution is 0.1 molar with respect to OH^- ion and is in equilibrium with solid $Pb(OH)_2$. What is the concentration of (a) the Pb^{++} ion, (b) the $HPbO_2^-$ ion, and (c) the H^+ ion in this solution?
18. Will .002 mole of $Cr(OH)_3$ dissolve in 1 liter of 0.1 molar NaOH?
19. Excess $Al(OH)_3$ is added to 1 liter of a solution of NaOH. After equilibrium is reached .01 mole of $Al(OH)_3$ is dissolved. What is the final concentration of the OH^- ion?
20. Write equations (17) and (18) in structural form, similar to equation (20).
21. Calculate the concentrations of the Cu^{++}, $HCuO_2^-$, and CuO_2^{--} ions in equilibrium with solid $Cu(OH)_2$ and with a NaOH solution for which the OH^- ion concentration is 0.1 *M*.

CHAPTER

13

Oxidation-Reduction Equilibria

In Chapter 5 we considered oxidation and reduction only from the standpoint of balancing equations, and we learned that any equation can be balanced just as easily when reversed, i.e., from right to left as well as from left to right. Therefore, the fact that an equation can be balanced does not mean that it necessarily proceeds as indicated. This question can be determined only by experiment. Experiments to determine the course of a reaction are made in a variety of ways. The commonest of these involves the use of electrical cells, but the detailed method by which such experiments are carried out is too involved for this course. It is possible to correlate all such equilibrium experiments in such a way that one hundred experiments will serve to determine the course of thousands of other reactions. In this chapter we shall see how this is done.

Relative Strengths of Oxidizing and Reducing Agents. The metals are regarded as good reducing agents since they all exhibit a tendency to lose electrons and form positive ions. This tendency varies considerably from metal to metal. The alkali and alkaline earth metals show a great tendency to lose electrons while this tendency is much less pronounced in the case of the noble metals such as platinum and gold. The so-called electromotive series of the elements is an arrangement based upon the tendency of elements to lose electrons and is accordingly also an arrangement of the elements as reducing agents. The alkali and alkaline earth metals are found

at the beginning while platinum and gold are at the end of the series of metals. Hydrogen occupies an intermediate position.

It is possible to determine the order of the metals in this series by displacement reactions, since the elements which show a great tendency to lose electrons and form positive ions will displace elements from solution which show this same tendency to a lesser degree. The following are a few familiar examples of displacement reactions:

$$Ca + Zn^{++} = Zn + Ca^{++} \quad (1)$$

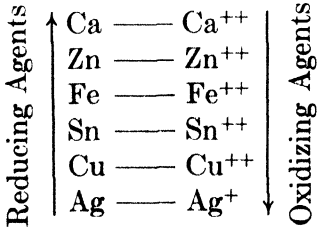
$$Zn + Fe^{++} = Fe + Zn^{++} \quad (2)$$

$$Fe + Sn^{++} = Sn + Fe^{++} \quad (3)$$

$$Sn + Cu^{++} = Cu + Sn^{++} \quad (4)$$

$$Cu + 2Ag^{+} = 2Ag + Cu^{++} \quad (5)$$

The order of the decreasing tendency of these elements to lose electrons is Ca, Zn, Fe, Sn, Cu, and Ag, which is also the decreasing order of these elements as reducing agents. Since every reducing agent must react with an oxidizing agent in an oxidation-reduction reaction, the ions of these particular elements are therefore the oxidizing agents. The ion of the best reducing agent is itself the poorest oxidizing agent, for if a metal has a great tendency to lose electrons its ion must have a small tendency to acquire them. When both the metal and its ion are listed as an oxidation-reduction couple we obtain a table of oxidizing and reducing agents as follows:



Most of the non-metals have a pronounced tendency to gain electrons, that is, to behave as oxidizing agents. Those elements which show a greater tendency to acquire electrons

and form negative ions will displace elements from solution which show this same tendency to a lesser degree. For example,

$$Cl_2 + 2Br^- = 2Cl^- + Br_2 \quad (6)$$

$$Br_2 + 2I^- = 2Br^- + I_2 \quad (7)$$

$$I_2 + H_2S = 2I^- + S + 2H^+ \quad (8)$$

As far as the ability to gain electrons is concerned these substances fall in the decreasing order of Cl_2, Br_2, I_2, and S. Sulfur is the weakest and chlorine the strongest oxidizing agent of this group. The ions of these elements may be regarded as reducing agents. On the basis of reactions which are known to take place between these non-metals and the metals, both may be included in a single table.

TABLE 26

OXIDATION-REDUCTION COUPLES

Reducing Agents		Oxidizing Agents
Ca	Ca^{++}	
Zn	Zn^{++}	
Fe	Fe^{++}	
Sn	Sn^{++}	
H_2S	$S + 2H^+$	
Cu	Cu^{++}	
I^-	I_2	
Ag	Ag^+	
Br^-	Br_2	
Cl^-	Cl_2	

Any substance on the right side of the table (oxidizing agent) will react with any substance on the left (reducing agent) provided that the reducing agent lies *above* the oxidizing agent. For example, iodine will react with zinc to produce iodide ion and zinc ion in solution.

$$I_2 + Zn = Zn^{++} + 2I^- \quad (9)$$

It has already been shown that oxidizing and reducing agents are not limited to the elements alone. Many ions of the elements and groups of elements (radicals) may take the

part of reducing and oxidizing agents. Thus MnO_4^- ion, in the presence of H^+ ion, will oxidize Fe^{++}, I^-, Cl^- and Br^- ions; $Cr_2O_7^{--}$ ion, in the presence of H^+ ion, will oxidize Br^-, I^- and many other ions; Sn^{++} ion will reduce NO_3^-, ClO^-, AsO_4^{---}, Bi^{+++}, Fe^{+++} and other ions.

Oxidation-Reduction Equilibria. Table 27, which is an extension of Table 26, includes all of the principal oxidizing and reducing agents commonly used in inorganic chemistry. By the use of this table, in conjunction with the tables which list the solubility product constants of difficultly soluble substances and the ionization constants for weak acids, it is possible to predict the course of more than 10,000 reactions. Such predictions may be made on a quantitative as well as a qualitative basis. In other words, it is possible to calculate the equilibrium constants for all of these oxidation-reduction reactions. To obtain some idea of the significance of Table 27, the meaning of the symbols involved, and the manner in which it was constructed, it is necessary to consider some specific oxidation-reduction equilibria.

Suppose, for example, that we consider the equilibrium between Fe^{++} ion, Fe^{+++} ion, H^+ ion and H_2, which is represented by the equation

$$2H^+ + 2Fe^{++} = H_2 + 2Fe^{+++} \qquad (10)$$

This oxidation-reduction reaction, as written in equation (10), involves an increase and decrease of two charges or two electrons. Dividing this equation by two in order to obtain an oxidation-reduction change of only one charge or one electron, we have

$$H^+ + Fe^{++} = \tfrac{1}{2}H_2 + Fe^{+++}* \qquad (11)$$

This equation represents an equilibrium which in every respect is like the equilibria discussed in previous chapters.

* In equation (11) the coefficient of H_2 is $\frac{1}{2}$. When considering any equation from the standpoint of molecules and single ions we eliminate all fractional coefficients. However, if the equation is interpreted in terms of moles it is quite permissible to use fractions. In this latter sense equation (11) is interpreted; one mole of hydrogen ion when reacting with one mole of ferrous ion produces one-half mole hydrogen gas and one mole ferric ion.

Likewise, the expression for the equilibrium constant will contain the concentrations of the products of the reaction in the numerator and the concentrations of the reactants in the denominator.

$$\frac{(H_2)^{\frac{1}{2}}(Fe^{+++})}{(H^+)(Fe^{++})} = K_{eq} = 10^{-13.1} * \qquad (12)$$

The value of the constant, $10^{-13.1}$, has been determined experimentally by measuring the pressure of the hydrogen gas (expressed in atmospheres) and the concentrations of the Fe^{++}, Fe^{+++} and H^+ ions (in terms of moles per liter of solution). In many oxidation-reduction reactions the equilibrium is displaced so far in one direction that the small concentrations of the reactants cannot be determined by ordinary analytical methods. However, in many cases the voltage delivered by an E.M.F. cell, consisting of the ions and molecules of an oxidation-reduction system in equilibrium, can be measured. This voltage depends upon the concentrations of the constituents of the oxidation-reduction equilibrium and serves as a means of determining the equilibrium constants for the reactions. Such cells are similar to the familiar Daniell cell. For our present purpose we shall omit any discussion of the analytical method of determining the concentrations of substances involved in equilibria of this kind.

In equation (12) there are two oxidation-reduction couples involved, namely, $\frac{1}{2}H_2 \text{ —— } H^+$ and $Fe^{++} \text{ —— } Fe^{+++}$. For convenience these couples are to be regarded as half-reactions, the equilibrium expressions for which are

$$\frac{(H_2)^{\frac{1}{2}}}{(H^+)} = K_1 \quad \text{and} \quad \frac{(Fe^{+++})}{(Fe^{++})} = K_2 \qquad (13)$$

It is impossible to obtain absolute values for the equilibrium constants for the half-reactions since oxidation can proceed only when accompanied by a reduction reaction and vice versa.

* $10^{-13.1}$ is a pure exponential number and is equal to $10^{+0.9} \times 10^{-14}$ which in turn is equal to 7.95×10^{-14}. For the present purpose it is very much more convenient to use these fractional exponents rather than mixed numbers. For a complete discussion of exponential numbers see the Appendix.

In this particular case Fe^{++} ion can be converted to Fe^{+++} ion only in the presence of an oxidizing agent which in equation (11) is the H^+ ion. The identical argument applies for the reduction process. However, if we could obtain ***relative*** values for the half-reactions it would then be possible to use combinations of these relative values to calculate equilibrium constants for oxidation-reduction reactions involving any two or more of the half-reactions. *Such a procedure is possible.*

To illustrate the significance of the half-reaction constants given in Table 27, let us consider the equilibrium expressions of equation (12). It is not possible to obtain a definite numerical value for either of the half-reaction constants, yet we can obtain ***relative*** values of these ratios by assuming some arbitrary value for one of them. For convenience, allow the ratio $\frac{(H_2)^{\frac{1}{2}}}{(H^+)}$ to be equal to $\frac{1}{\alpha}$, i.e., the inverse of this ratio $\frac{(H^+)}{(H_2)^{\frac{1}{2}}}$, to be equal to α. Substituting this value in equation (12) we obtain $10^{-13\,1}\alpha$ for the value of the ratio $\frac{(Fe^{+++})}{(Fe^{++})}$ since

$$\frac{(H_2)^{\frac{1}{2}}}{(H^+)} \times \frac{(Fe^{+++})}{(Fe^{++})} = \frac{1}{\alpha} \times \frac{(Fe^{+++})}{(Fe^{++})} = 10^{-13\,1}$$

and

$$\frac{(Fe^{+++})}{(Fe^{++})} = 10^{-13\,1}\alpha$$

Now consider another reaction involving Fe^{++} and Fe^{+++} ions.

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O \quad (14)$$

This equation involves an oxidation-reduction change of five units of charge or five electrons. Changing equation (14) so that only one unit of charge, or one electron, is involved, we have

$$\tfrac{1}{5}MnO_4^- + Fe^{++} + \tfrac{8}{5}H^+ = \tfrac{1}{5}Mn^{++} + Fe^{+++} + \tfrac{4}{5}H_2O \quad (15)$$

The equilibrium constant for this reaction is

$$\frac{(Fe^{+++})(Mn^{++})^{\frac{1}{5}}H_2O^{\frac{4}{5}}}{(Fe^{++})(MnO_4^-)^{\frac{1}{5}}(H^+)^{\frac{8}{5}}} = K_{eq} = 10^{12\,5} \text{ (experimental)} \quad (16)$$

In this expression we have included the term $H_2O^{\frac{4}{5}}$ where normally it would be omitted, as in past examples, for the concentration of the water molecules does not change appreciably in such reactions and for all practical purposes may be regarded as remaining constant. Although the term can be omitted from equation (16) we shall see later that its inclusion will be very convenient in the selection of the proper half-reactions required for the calculation of the oxidation-reduction equilibrium constants in question. All such terms which can be omitted appear in *italics*. Formally each of these *italicized* terms may be regarded as being equal to unity. Substances which do not change appreciably in concentration during the course of a reaction, such as water, and all substances existing in a separate phase (not in solution), such as relatively insoluble solids, come under this classification.

The value of the term $\frac{(Fe^{+++})}{(Fe^{++})}$ was previously found to be equal to $10^{-13\ 1}\alpha$ (maintaining the value $\frac{(H^+)}{(H_2)^{\frac{1}{2}}}$ as α). Thus,

$$\frac{(Fe^{+++})}{(Fe^{++})} \times \frac{(Mn^{++})^{\frac{1}{5}} H_2O^{\frac{4}{5}}}{(MnO_4^-)^{\frac{1}{5}}(H^+)^{\frac{8}{5}}} = 10^{-13\ 1}\alpha \times \frac{(Mn^{++})^{\frac{1}{5}} H_2O^{\frac{4}{5}}}{(MnO_4^-)^{\frac{1}{5}}(H^+)^{\frac{8}{5}}} = 10^{12\ 5}$$

and therefore

$$\frac{(Mn^{++})^{\frac{1}{5}} H_2O^{\frac{4}{5}}}{(MnO_4^-)^{\frac{1}{5}}(H^+)^{\frac{8}{5}}} = \frac{10^{12.5}}{10^{-13\ 1}\alpha} = \frac{10^{25\ 6}}{\alpha}$$

The inverse of this value is $10^{-25\ 6}\alpha$, as given in Table 27.

We shall next consider the reaction represented by the equation

$$3Fe^{++} + NO_3^- + 4H^+ = 3Fe^{+++} + NO + 2H_2O \qquad (17)$$

Reducing this equation to represent one electron change, we have

$$Fe^{++} + \tfrac{1}{3}NO_3^- + \tfrac{4}{3}H^+ = Fe^{+++} + \tfrac{1}{3}NO + \tfrac{2}{3}H_2O \qquad (18)$$

the value for the equilibrium constant of which is

$$\frac{(Fe^{+++})(NO)^{\frac{1}{3}} H_2O^{\frac{2}{3}}}{(Fe^{++})(NO_3^-)^{\frac{1}{3}}(H^+)^{\frac{4}{3}}} = 10^{3.1}\ \text{(experimental)} \qquad (19)$$

Since $\frac{(Fe^{+++})}{(Fe^{++})}$ equals $10^{-13.1}\alpha$, the value for $\frac{(NO_3^-)^{\frac{1}{3}}(H^+)^{\frac{4}{3}}}{(NO)^{\frac{1}{3}}H_2O^{\frac{2}{3}}}$ is accordingly $10^{-16.2}\alpha$, as given in Table 27.

In this way it is possible to build up values for the half-reaction constants for all oxidation-reduction couples. It will be observed that for every completed reaction the alphas (α's) always cancel. The reason for reducing every half-reaction to one which involves a change of only one unit of charge or one electron is to allow for this cancellation. Since the alpha term always cancels it can be omitted. The values of the half-reaction constants in Table 27 therefore include only the coefficients of alpha.

TABLE 27

OXIDATION-REDUCTION HALF-REACTIONS

For convenience in locating the half-reaction in the table,* each equation is given in terms of whole number coefficients. The equilibrium expression for the half-reaction, however, is for a one electron loss, or a gain of one unit of valence number. The exponent of the half-reaction constant is given to the first place following the decimal point. In some cases the experimental data for the determination of this value do not warrant a significant figure of this magnitude, while in other cases they do. Therefore the figure following the decimal point is not always significant; it represents an estimated value of the average accuracy. For convenience, the solid phases such as *Li* and the practically non-varying components such as H_2O are included in the equilibrium expressions for the half-reactions and appear in *italics*. These will either cancel in the calculated equilibrium expression for a complete reaction or they are to be omitted after the equilibrium expression has been finally set up. They are included here for convenience in manipulating the half-reaction expressions. The exponents for the solid and non-varying components have no significance. These are also included for convenience. The concentrations of gases, for example (H_2), are to be expressed in terms of pressures (atmospheres).

* Compiled from data obtained from *Oxidation Potentials*, by Wendell M. Latimer (Prentice-Hall), Second Edition, 1952, and by correspondence with the author.

As in Table 26 the right-hand member of each half-reaction is an oxidizing agent, and the left-hand member a reducing agent. The best reducing agents are at the beginning of the table and the best oxidizing agents at the end. Any given oxidizing agent will oxidize any reducing agent lying above it in this table.

It is possible to predict qualitatively whether or not some of the simpler reactions will proceed merely by inspecting the relative positions of the appropriate half-reactions in the table. In many cases, however, the complete reaction in question will involve more than two half-reactions. Under such conditions a quantitative calculation of the equilibrium constant is necessary. In any event the extent to which a given reaction will proceed can only be determined by making a quantitative calculation involving the half-reaction constants.

Half-Reaction	Equilibrium Expression	Value of Constant
1. $Li \rightleftharpoons Li^+$	$\frac{(Li^+)}{Li}$	$10^{51.5}$
2. $Rb \rightleftharpoons Rb^+$	$\frac{(Rb^+)}{Rb}$	$10^{49.4}$
3. $K \rightleftharpoons K^+$	$\frac{(K^+)}{K}$	$10^{49.4}$
4. $Ba \rightleftharpoons Ba^{++}$	$\frac{(Ba^{++})^{\frac{1}{2}}}{Ba^{\frac{1}{2}}}$	$10^{49.0}$
5. $Sr \rightleftharpoons Sr^{++}$	$\frac{(Sr^{++})^{\frac{1}{2}}}{Sr^{\frac{1}{2}}}$	$10^{48.8}$
6. $Ca \rightleftharpoons Ca^{++}$	$\frac{(Ca^{++})^{\frac{1}{2}}}{Ca^{\frac{1}{2}}}$	$10^{48.5}$
7. $Na \rightleftharpoons Na^+$	$\frac{(Na^+)}{Na}$	$10^{46.9}$
8. $Mg \rightleftharpoons Mg^{++}$	$\frac{(Mg^{++})^{\frac{1}{2}}}{Mg}$	$10^{40.1}$
9. $Al \rightleftharpoons Al^{+++}$	$\frac{(Al^{+++})^{\frac{1}{3}}}{Al^{\frac{1}{3}}}$	$10^{28.1}$
10. $Mn \rightleftharpoons Mn^{++}$	$\frac{(Mn^{++})^{\frac{1}{2}}}{Mn^{\frac{1}{2}}}$	$10^{19.9}$

Half-Reaction	Equilibrium Expression	Value of Constant
11. $CN^- + 2OH^- \text{ —— } CNO^- + H_2O$	$\frac{(CNO^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(CN^-)^{\frac{1}{2}}(OH^-)}$	$10^{16.4}$
12. $SO_3^{--} + 2OH^- \text{ —— } SO_4^{--} + H_2O$	$\frac{(SO_4^{--})^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(SO_3^{--})^{\frac{1}{2}}(OH^-)}$	$10^{15.7}$
13. $Cr \text{ —— } Cr^{++}$	$\frac{(Cr^{++})^{\frac{1}{2}}}{Cr^{\frac{1}{2}}}$	$10^{15.4}$
14. $H_2 + 2OH^- \text{ —— } 2H_2O$	$\frac{H_2O}{(H_2)^{\frac{1}{2}}(OH^-)}$	$10^{14.0}$
15. $Zn \text{ —— } Zn^{++}$	$\frac{(Zn^{++})^{\frac{1}{2}}}{Zn^{\frac{1}{2}}}$	$10^{12.9}$
16. $Cr \text{ —— } Cr^{+++}$	$\frac{(Cr^{+++})^{\frac{1}{3}}}{Cr^{\frac{1}{3}}}$	$10^{12.5}$
17. $H_2Te \text{ —— } Te + 2H^+$	$\frac{Te^{\frac{1}{2}}(H^+)}{(H_2Te)^{\frac{1}{2}}}$	$10^{12.2}$
18. $Ga \text{ —— } Ga^{+++}$	$\frac{(Ga^{+++})^{\frac{1}{3}}}{Ga^{\frac{1}{3}}}$	$10^{9.0}$
19. $S^{--} \text{ —— } S$	$\frac{S^{\frac{1}{2}}}{(S^{--})^{\frac{1}{2}}}$	$10^{7.9}$
20. $Fe \text{ —— } Fe^{++}$	$\frac{(Fe^{++})^{\frac{1}{2}}}{Fe^{\frac{1}{2}}}$	$10^{7.4}$
21. $Cr^{++} \text{ —— } Cr^{+++}$	$\frac{(Cr^{+++})}{(Cr^{++})}$	$10^{6.9}$
22. $Cd \text{ —— } Cd^{++}$	$\frac{(Cd^{++})^{\frac{1}{2}}}{Cd^{\frac{1}{2}}}$	$10^{6.8}$
23. $H_2Se \text{ —— } Se + 2H^+$	$\frac{Se^{\frac{1}{2}}(H^+)}{(H_2Se)^{\frac{1}{2}}}$	$10^{6.8}$
24. $Ti^{++} \text{ —— } Ti^{+++}$	$\frac{(Ti^{+++})}{(Ti^{++})}$	$10^{6.3}$
25. $Pb + SO_4^{--} \text{ —— } PbSO_4$	$\frac{PbSO_4^{\frac{1}{2}}}{Pb^{\frac{1}{2}}(SO_4^{--})^{\frac{1}{2}}}$	$10^{6.0}$
26. $In \text{ —— } In^{+++}$	$\frac{(In^{+++})^{\frac{1}{3}}}{In^{\frac{1}{3}}}$	$10^{5.8}$

Half-Reaction	Equilibrium Expression	Value of Constant
27. $Tl \rightleftharpoons Tl^{+}$	$\frac{(Tl^{+})}{Tl}$	$10^{5.7}$
28. $Co \rightleftharpoons Co^{++}$	$\frac{(Co^{++})^{\frac{1}{2}}}{Co^{\frac{1}{2}}}$	$10^{4.7}$
29. $H_3PO_3 \rightleftharpoons H_3PO_4 + 2H^{+}$	$\frac{(H_3PO_4)^{\frac{1}{2}}(H^{+})}{(H_3PO_3)^{\frac{1}{2}}}$	$10^{4.7}$
30. $Ni \rightleftharpoons Ni^{++}$	$\frac{(Ni^{++})^{\frac{1}{2}}}{Ni^{\frac{1}{2}}}$	$10^{4.3}$
31. $S_2O_6^{--} \rightleftharpoons 2SO_4^{--} + 4H^{+}$	$\frac{(SO_4^{--})(H^{+})^2}{(S_2O_6^{--})^{\frac{1}{2}}}$	$10^{3.7}$
32. $Sn \rightleftharpoons Sn^{++}$	$\frac{(Sn^{++})^{\frac{1}{2}}}{Sn^{\frac{1}{2}}}$	$10^{2.3}$
33. $Pb \rightleftharpoons Pb^{++}$	$\frac{(Pb^{++})^{\frac{1}{2}}}{Pb^{\frac{1}{2}}}$	$10^{2.1}$
34. $9OH^{-} + NH_3 \rightleftharpoons NO_3^{-} + 6H_2O$	$\frac{(NO_3^{-})^{\frac{1}{8}}H_2O^{\frac{6}{8}}}{(OH^{-})^{\frac{9}{8}}(NH_3)^{\frac{1}{8}}}$	$10^{2.0}$
35. $Cu_2O + 2OH^{-} \rightleftharpoons 2CuO + H_2O$	$\frac{CuO\ H_2O^{\frac{1}{2}}}{Cu_2O^{\frac{1}{2}}(OH^{-})}$	$10^{1.4}$
36. $HO_2^{-} + OH^{-} \rightleftharpoons O_2 + H_2O$	$\frac{(O_2)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(HO_2^{-})^{\frac{1}{2}}(OH^{-})^{\frac{1}{2}}}$	$10^{1.3}$
37. $Mn(OH)_2 + 2OH^{-} \rightleftharpoons MnO_2 + H_2O$	$\frac{MnO_2^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{Mn(OH)_2^{\frac{1}{2}}(OH^{-})}$	$10^{0.8}$
38. $H_2 \rightleftharpoons 2H^{+}$	$\frac{(H^{+})}{(H_2)^{\frac{1}{2}}}$	10^{0}
39. $NO_2^{-} + 2OH^{-} \rightleftharpoons NO_3^{-} + H_2O$	$\frac{(NO_3^{-})^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(NO_2^{-})^{\frac{1}{2}}(OH^{-})}$	$10^{-0.2}$
40. $2S_2O_3^{--} \rightleftharpoons S_4O_6^{--}$	$\frac{(S_4O_6^{--})^{\frac{1}{2}}}{(S_2O_3^{--})}$	$10^{-1.4}$
41. $Co(NH_3)_6^{++} \rightleftharpoons Co(NH_3)_6^{+++}$	$\frac{(Co(NH_3)_6^{+++})}{(Co(NH_3)_6^{++})}$	$10^{-1.7}$
42. $Mn(OH)_2 \rightleftharpoons Mn(OH)_3$	$\frac{Mn(OH)_3}{Mn(OH)_2}$	$10^{-1.7}$

Half-Reaction	Equilibrium Expression	Value of Constant
43. $Ti^{+++} + H_2O \text{ —— } TiO^{++} + 2H^+$	$\frac{(TiO^{++})(H^+)^2}{(Ti^{+++})H_2O}$	$10^{-1.7}$
44. $H_2S \text{ —— } S + 2H^+$	$\frac{S^{\frac{1}{2}}(H^+)}{(H_2S)^{\frac{1}{2}}}$	$10^{-2.4}$
45. $Sn^{++} \text{ —— } Sn^{++++}$	$\frac{(Sn^{++++})^{\frac{1}{2}}}{(Sn^{++})^{\frac{1}{2}}}$	$10^{-2.5}$
46. $2Sb + 3H_2O \text{ —— } Sb_2O_3 + 6H^+$	$\frac{Sb_2O_3^{\frac{1}{6}}(H^+)}{Sb^{\frac{1}{3}}H_2O^{\frac{1}{2}}}$	$10^{-2.6}$
47. $Cu^+ \text{ —— } Cu^{++}$	$\frac{(Cu^{++})}{(Cu^+)}$	$10^{-2.6}$
48. $Bi + H_2O + Cl^- \text{ —— } BiOCl + 2H^+$	$\frac{BiOCl^{\frac{1}{3}}(H^+)^{\frac{2}{3}}}{Bi^{\frac{1}{3}}H_2O^{\frac{1}{3}}(Cl^-)^{\frac{1}{3}}}$	$10^{-2.7}$
49. $H_2SO_3 + H_2O \text{ —— } SO_4^{--} + 4H^+$	$\frac{(SO_4^{--})^{\frac{1}{2}}(H^+)^2}{(H_2SO_3)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-2.9}$
50. $Co(OH)_2 + OH^- \text{ —— } Co(OH)_3$	$\frac{Co(OH)_3}{Co(OH)_2(OH^-)}$	$10^{-2.9}$
51. $Hg + 4Br^- \text{ —— } HgBr_4^{--}$	$\frac{(HgBr_4^{--})^{\frac{1}{2}}}{Hg^{\frac{1}{2}}(Br^-)^2}$	$10^{-3.5}$
52. $Ag + Cl^- \text{ —— } AgCl$	$\frac{AgCl}{Ag(Cl^-)}$	$10^{-3.8}$
53. $As + 2H_2O \text{ —— } HAsO_2 + 3H^+$	$\frac{(HAsO_2)^{\frac{1}{3}}(H^+)}{As^{\frac{1}{3}}H_2O^{\frac{2}{3}}}$	$10^{-4.2}$
54. $PbO + 2OH^- \text{ —— } PbO_2 + H_2O$	$\frac{PbO_2^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{PbO^{\frac{1}{2}}(OH^-)}$	$10^{-4.2}$
55. $I^- + 6OH^- \text{ —— } IO_3^- + 3H_2O$	$\frac{(IO_3^-)^{\frac{1}{6}}H_2O^{\frac{1}{2}}}{(I^-)^{\frac{1}{6}}(OH^-)}$	$10^{-4.4}$
56. $Bi + H_2O \text{ —— } BiO^+ + 2H^+$	$\frac{(BiO^+)^{\frac{1}{3}}(H^+)^{\frac{2}{3}}}{Bi^{\frac{1}{3}}H_2O^{\frac{1}{3}}}$	$10^{-5.4}$
57. $ClO_2^- + 2OH^- \text{ —— } ClO_3^- + H_2O$	$\frac{(ClO_3^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(ClO_2^-)^{\frac{1}{2}}(OH^-)}$	$10^{-5.6}$
58. $U^{++++} + 2H_2O \text{ —— } UO_2^{++} + 4H^+$	$\frac{(UO_2^{++})^{\frac{1}{2}}(H^+)^2}{(U^{++++})^{\frac{1}{2}}H_2O}$	$10^{-5.6}$

	Half-Reaction	Equilibrium Expression	Value of Constant
59.	$Cu \rightleftharpoons Cu^{++}$	$\frac{(Cu^{++})^{\frac{1}{2}}}{Cu^{\frac{1}{2}}}$	$10^{-5.6}$
60.	$2Ag + 2OH^- \rightleftharpoons Ag_2O + H_2O$	$\frac{Ag_2O^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{Ag(OH^-)}$	$10^{-5.6}$
61.	$ClO_3^- + 2OH^- \rightleftharpoons ClO_4^- + H_2O$	$\frac{(ClO_4^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(ClO_3^-)^{\frac{1}{2}}(OH^-)}$	$10^{-5.8}$
62.	$Fe(CN)_6^{----} \rightleftharpoons Fe(CN)_6^{---}$	$\frac{(Fe(CN)_6^{---})}{(Fe(CN)_6^{----})}$	$10^{-6.1}$
63.	$V^{+++} + H_2O \rightleftharpoons VO^{++} + 2H^+$	$\frac{(VO^{++})^{\frac{1}{2}}(H^+)}{(VO^{+++})^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-6.1}$
64.	$S_2O_3^{--} + 3H_2O \rightleftharpoons 2H_2SO_3 + 2H^+$	$\frac{(H_2SO_3)^{\frac{2}{4}}(H^+)^{\frac{2}{4}}}{(S_2O_3^{--})^{\frac{1}{4}}H_2O^{\frac{3}{4}}}$	$10^{-6.8}$
65.	$OH^- + HO_2^- \rightleftharpoons O_2^- + H_2O$	$\frac{(O_2^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(OH^-)^{\frac{1}{2}}(HO_2^-)^{\frac{1}{2}}}$	$10^{-6.8}$
66.	$4OH^- \rightleftharpoons O_2 + 2H_2O$	$\frac{(O_2)^{\frac{1}{4}}H_2O^{\frac{2}{4}}}{(OH^-)}$	$10^{-6.8}$
67.	$S + 3H_2O \rightleftharpoons H_2SO_3 + 4H^+$	$\frac{(H_2SO_3)^{\frac{1}{4}}(H^+)}{S^{\frac{1}{4}}H_2O^{\frac{3}{4}}}$	$10^{-7.6}$
68.	$Ni(OH)_2 + 2OH^- \rightleftharpoons NiO_2 + 2H_2O$	$\frac{NiO_2^{\frac{1}{2}}H_2O}{Ni(OH)_2^{\frac{1}{2}}(OH^-)}$	$10^{-8.3}$
69.	$I^- + 2OH^- \rightleftharpoons IO^- + H_2O$	$\frac{(IO^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(I^-)^{\frac{1}{2}}(OH^-)}$	$10^{-8.3}$
70.	$Cu \rightleftharpoons Cu^+$	$\frac{(Cu^+)}{Cu}$	$10^{-8.8}$
71.	$Te + 2H_2O \rightleftharpoons TeO_2 + 4H^+$	$\frac{TeO_2^{\frac{1}{4}}(H^+)}{Te^{\frac{1}{4}}H_2O^{\frac{2}{4}}}$	$10^{-8.9}$
72.	$2I^- \rightleftharpoons I_2$	$\frac{I_2^{\frac{1}{2}}}{(I^-)}$	$10^{-9.1}$
73.	$CuCl \rightleftharpoons Cu^{++} + Cl^-$	$\frac{(Cu^{--})(Cl^-)}{CuCl}$	$10^{-9.1}$
74.	$HAsO_2 + 2H_2O \rightleftharpoons H_3AsO_4 + 2H^+$	$\frac{(H_3AsO_4)^{\frac{1}{2}}(H^+)}{(HAsO_2)^{\frac{1}{2}}H_2O}$	$10^{-9.5}$

	Half-Reaction	Equilibrium Expression	Value of Constant
75.	$MnO_4^{--} \rightleftharpoons MnO_4^-$	$\frac{(MnO_4^-)}{(MnO_4^{--})}$	$10^{-9.5}$
76.	$Ag_2O + 2OH^- \rightleftharpoons 2AgO + H_2O$	$\frac{AgOH_2O^{\frac{1}{2}}}{Ag_2O^{\frac{1}{2}}(OH^-)}$	$10^{-9.6}$
77.	$2SbO^+ + 3H_2O \rightleftharpoons Sb_2O_5 + 6H^+$	$\frac{Sb_2O_5^{\frac{1}{4}}(H^+)^{\frac{6}{4}}}{(SbO^+)^{\frac{2}{4}}H_2O^{\frac{3}{4}}}$	$10^{-9.8}$
78.	$MnO_2 + 4OH^- \rightleftharpoons MnO_4^{--} + 2H_2O$	$\frac{(MnO_4^{--})^{\frac{1}{2}}H_2O}{MnO_2^{\frac{1}{2}}(OH^-)^2}$	$10^{-10.1}$
79.	$Br^- + 6OH^- \rightleftharpoons BrO_3^- + 3H_2O$	$\frac{(BrO_3^-)^{\frac{1}{6}}H_2O^{\frac{3}{6}}}{(Br^-)^{\frac{1}{6}}(OH^-)}$	$10^{-10.5}$
80.	$U^{++++} + 2H_2O \rightleftharpoons UO_2^{++} + 2H^+$	$\frac{(UO_2^{++})^{\frac{1}{2}}(H^+)}{(U^{++++})^{\frac{1}{2}}H_2O}$	$10^{-10.5}$
81.	$CuBr \rightleftharpoons Cu^{++} + Br^-$	$\frac{(Cu^{++})(Br^-)}{CuBr}$	$10^{-10.9}$
82.	$ClO^- + 2OH^- \rightleftharpoons ClO_2^- + H_2O$	$\frac{(ClO_2^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(ClO^-)^{\frac{1}{2}}(OH^-)}$	$10^{-11.2}$
83.	$H_2O_2 \rightleftharpoons O_2 + 2H^+$	$\frac{(O_2)^{\frac{1}{2}}(H^+)}{(H_2O_2)^{\frac{1}{2}}}$	$10^{-11.6}$
84.	$Se + 3H_2O \rightleftharpoons H_2SeO_3 + 4H^+$	$\frac{(H_2SeO_3)^{\frac{1}{4}}(H^+)}{Se^{\frac{1}{4}}H_2O^{\frac{3}{4}}}$	$10^{-12.5}$
85.	$Br^- + 2OH^- \rightleftharpoons BrO^- + H_2O$	$\frac{(BrO^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(Br^-)^{\frac{1}{2}}(OH^-)}$	$10^{-12.9}$
86.	$Fe^{++} \rightleftharpoons Fe^{+++}$	$\frac{(Fe^{+++})}{(Fe^{++})}$	$10^{-13.1}$
87.	$2Hg \rightleftharpoons Hg_2^{++}$	$\frac{(Hg_2^{++})^{\frac{1}{2}}}{Hg}$	$10^{-13.3}$
88.	$Ag \rightleftharpoons Ag^+$	$\frac{(Ag^+)}{Ag}$	$10^{-13.5}$
89.	$N_2O_4 + 2H_2O \rightleftharpoons 2NO_3^- + 4H^+$	$\frac{(NO_3^-)(H^+)^2}{(N_2O_4)^{\frac{1}{2}}H_2O}$	$10^{-13.5}$
90.	$3OH^- \rightleftharpoons HO_2^- + H_2O$	$\frac{(HO_2^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(OH^-)^{\frac{3}{2}}}$	$10^{-14.9}$

	Half-Reaction	Equilibrium Expression	Value of Constant
91.	$Cl^- + 2OH^- \text{ — } ClO^- + H_2O$	$\frac{(ClO^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(Cl^-)^{\frac{1}{2}}(OH^-)}$	$10^{-15.1}$
92.	$NH_4^+ + 3H_2O \text{ — } NO_3^- + 10H^+$	$\frac{(NO_3^-)^{\frac{1}{8}}(H^+)^{\frac{10}{8}}}{(NH_4^+)^{\frac{1}{8}}H_2O^{\frac{3}{4}}}$	$10^{-15.3}$
93.	$Hg_2^{++} \text{ — } 2Hg^{++}$	$\frac{(Hg^{++})}{(Hg_2^{++})^{\frac{1}{2}}}$	$10^{-15.5}$
94.	$HNO_2 + H_2O \text{ — } NO_3^- + 3H^+$	$\frac{(NO_3^-)^{\frac{1}{2}}(H^+)^{\frac{3}{2}}}{(HNO_2)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-15.9}$
95.	$NO + 2H_2O \text{ — } NO_3^- + 4H^+$	$\frac{(NO_3^-)^{\frac{1}{3}}(H^+)^{\frac{4}{3}}}{(NO)^{\frac{1}{3}}H_2O^{\frac{2}{3}}}$	$10^{-16.2}$
96.	$NO + H_2O \text{ — } HNO_2 + H^+$	$\frac{(HNO_2)(H^+)}{(NO)H_2O}$	$10^{-16.9}$
97.	$2Br^- \text{ — } Br_2$	$\frac{(Br_2)^{\frac{1}{2}}}{(Br^-)}$	$10^{-17.9}$
98.	$H_2SeO_3 + H_2O \text{ — } SeO_4^{--} + 4H^+$	$\frac{(SeO_4^{--})^{\frac{1}{2}}(H^+)^2}{(H_2SeO_3)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-19.4}$
99.	$ClO_3^- + H_2O \text{ — } ClO_4^- + 2H^+$	$\frac{(ClO_4^-)^{\frac{1}{2}}(H^+)}{(ClO_3^-)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-2.10}$
100.	$HClO_2 + H_2O \text{ — } ClO_3^- + 3H^+$	$\frac{(ClO_3^-)^{\frac{1}{2}}(H^+)^{\frac{3}{2}}}{(HClO_2)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-20.5}$
101.	$2H_2O \text{ — } O_2 + 4H^+$	$\frac{(O_2)^{\frac{1}{2}}(H^+)}{H_2O^{\frac{1}{2}}}$	$10^{-20.8}$
102.	$Mn^{++} + 2H_2O \text{ — } MnO_2 + 4H^+$	$\frac{MnO_2^{\frac{1}{2}}(H^+)^2}{(Mn^{++})^{\frac{1}{2}}H_2O}$	$10^{-20.8}$
103.	$O_2 + 2OH^- \text{ — } O_3 + H_2O$	$\frac{(O_3)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}{(O_2)^{\frac{1}{2}}(OH^-)}$	$10^{-21.0}$
104.	$Tl^+ \text{ — } Tl^{+++}$	$\frac{(Tl^{+++})^{\frac{1}{2}}}{(Tl^+)^{\frac{1}{2}}}$	$10^{-21.2}$
105.	$N_2O + 3H_2O \text{ — } 2HNO_2 + 4H^+$	$\frac{(HNO_2)^{\frac{1}{2}}(H^+)}{(N_2O)^{\frac{1}{4}}H_2O^{\frac{3}{4}}}$	$10^{-21.8}$
106.	$2Cr^{+++} + 7H_2O \text{ — } Cr_2O_7^{--} + 14H^+$	$\frac{(Cr_2O_7^{--})^{\frac{1}{6}}(H^+)^{\frac{14}{6}}}{(Cr^{+++})^{\frac{2}{6}}H_2O^{\frac{7}{6}}}$	$10^{-22.5}$

	Half-Reaction	Equilibrium Expression	Value of Constant
107.	$2Cl^- \text{—} Cl_2$	$\frac{(Cl_2)^{\frac{1}{2}}}{(Cl^-)}$	$10^{-23.0}$
108.	$Au + 3H_2O \text{—} Au(OH)_3 + 3H^+$	$\frac{(Au(OH)_3)^{\frac{1}{3}}(H^+)}{Au^{\frac{1}{3}}H_2O}$	$10^{-24.5}$
109.	$\frac{1}{2}I_2 + H_2O \text{—} HIO + H^+$	$\frac{(HIO)(H^+)}{(I_2)^{\frac{1}{2}}H_2O}$	$10^{-24.5}$
110.	$Pb^{++} + 2H_2O \text{—} PbO_2 + 4H^+$	$\frac{PbO_2^{\frac{1}{2}}(H^+)^2}{(Pb^{++})^{\frac{1}{2}}H_2O}$	$10^{-24.6}$
111.	$Au \text{—} Au^{+++}$	$\frac{(Au^{+++})^{\frac{1}{3}}}{Au^{\frac{1}{3}}}$	$10^{-25.4}$
112.	$Mn^{++} \text{—} Mn^{+++}$	$\frac{(Mn^{+++})}{(Mn^{++})}$	$10^{-25.6}$
113.	$Mn^{++} + 4H_2O \text{—} MnO_4^- + 8H^+$	$\frac{(MnO_4^-)^{\frac{1}{5}}(H^+)^{\frac{8}{5}}}{(Mn^{++})^{\frac{1}{5}}H_2O^{\frac{4}{5}}}$	$10^{-25.6}$
114.	$\frac{1}{2}Br_2 + 3H_2O \text{—} BrO_3^- + 6H^+$	$\frac{(BrO_3^-)^{\frac{1}{5}}(H^+)^{\frac{6}{5}}}{(Br_2)^{\frac{1}{10}}H_2O^{\frac{3}{5}}}$	$10^{-25.8}$
115.	$\frac{1}{2}Br_2 + H_2O \text{—} HBrO + H^+$	$\frac{(HBrO)(H^+)}{(Br_2)^{\frac{1}{2}}H_2O}$	$10^{-26.9}$
116.	$Ce^{+++} \text{—} Ce^{++++}$	$\frac{(Ce^{++++})}{(Ce^{+++})}$	$10^{-27.2}$
117.	$\frac{1}{2}Cl_2 + H_2O \text{—} HClO + H^+$	$\frac{(HClO)(H^+)}{(Cl_2)^{\frac{1}{2}}H_2O}$	$10^{-27.5}$
118.	$HClO + H_2O \text{—} HClO_2 + 2H^+$	$\frac{(HClO_2)^{\frac{1}{2}}(H^+)}{(HClO)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-27.7}$
119.	$Au \text{—} Au^+$	$\frac{(Au^+)}{Au}$	$10^{-28.4}$
120.	$Ni^{++} + 2H_2O \text{—} NiO_2 + 4H^+$	$\frac{NiO_2^{\frac{1}{2}}(H^+)^2}{(Ni^{++})^{\frac{1}{2}}H_2O}$	$10^{-28.4}$
121.	$PbSO_4 + 2H_2O \text{—} PbO_2 + SO_4^{--} + 4H^+$	$\frac{PbO_2^{\frac{1}{2}}(SO_3^{--})^{\frac{1}{2}}(H^+)^2}{PbSO_4^{\frac{1}{2}}H_2O}$	$10^{-28.4}$
122.	$MnO_2 + 2H_2O \text{—} MnO_4^- + 4H^+$	$\frac{(MnO_4^-)^{\frac{1}{3}}(H^+)^{\frac{4}{3}}}{MnO_2^{\frac{1}{3}}H_2O^{\frac{2}{3}}}$	$10^{-28.7}$

Half-Reaction	Equilibrium Expression	Value of Constant
123. $2H_2O \rightleftharpoons H_2O_2 + 2H^+$	$\frac{(H_2O_2)^{\frac{1}{2}}(H^+)}{H_2O}$	$10^{-29.9}$
124. $Co^{++} \rightleftharpoons Co^{+++}$	$\frac{(Co^{+++})}{(Co^{++})}$	$10^{-30.8}$
125. $Fe^{+++} + 4H_2O \rightleftharpoons FeO_4^{--} + 8H^+$	$\frac{(FeO_4^{--})^{\frac{1}{3}}(H^+)^{\frac{8}{3}}}{(Fe^{+++})^{\frac{1}{3}}H_2O^{\frac{4}{3}}}$	$10^{-32.1}$
126. $2SO_4^{--} \rightleftharpoons S_2O_8^{--}$	$\frac{(S_2O_8^{--})^{\frac{1}{2}}}{(SO_4^{--})}$	$10^{-34.0}$
127. $O_2 + H_2O \rightleftharpoons O_3 + 2H^+$	$\frac{(O_3)^{\frac{1}{2}}(H^+)}{(O_2)^{\frac{1}{2}}H_2O^{\frac{1}{2}}}$	$10^{-35.0}$
128. $2F^- \rightleftharpoons F_2$	$\frac{(F_2)^{\frac{1}{2}}}{(F^-)}$	$10^{-44.8}$
129. $2HF \rightleftharpoons F_2 + 2H^+$	$\frac{(F_2)^{\frac{1}{2}}(H^+)}{(HF)}$	$10^{-51.7}$

Examples to Illustrate Use of Table 27

Example 1.

Is it possible for hydrochloric acid to dissolve copper to form hydrogen gas and cupric ion? We know from experience that it is not possible. While a qualitative examination of the relative positions of the couples in the table above will give us this information, we may confirm this fact and observation by a calculation which uses the values given in the table for the equilibria involved. The equation for this reaction is

$$Cu + 2H^+ = Cu^{++} + H_2 \tag{1}$$

The corresponding equilibrium expression is

$$\frac{(Cu^{++})(H_2)}{Cu(H^+)^2} = K_{eq} \tag{2}$$

From the table we find that $\frac{(Cu^{++})^{\frac{1}{2}}}{Cu^{\frac{1}{2}}}$ has a value of $10^{-5.6}$ and $\frac{(H_2)^{\frac{1}{2}}}{(H^+)}$ the value of 10^0 or 1. Combining these two half-reaction expressions, we obtain

$$\frac{(Cu^{++})^{\frac{1}{2}}}{Cu^{\frac{1}{2}}} \times \frac{(H_2)^{\frac{1}{2}}}{(H^+)} = 10^{-5.6} \times 10^0 = 10^{-5.6} \tag{3}$$

Squaring both sides of equation (3) we obtain equation (4) with a numerical value for the constant of $10^{-11.2}$. Then omitting *Cu*, since it is in the solid phase, we obtain

$$\frac{(Cu^{++})(H_2)}{(H^+)^2} = K_{eq} = 10^{-11.2} \tag{4}$$

The small value of this constant indicates that this reaction will not proceed from left to right to any appreciable extent. If the value of any equilibrium constant were 1, then the reaction would proceed about halfway toward completion before equilibrium would be reached. At this point the concentrations of the products would be of the same order of magnitude as the concentrations of the reactants. If the constant were greater than 1, the concentrations of the products must exceed those of the reactants at equilibrium and therefore the reaction would proceed to a greater extent to the right. When the value of the constant is less than 1, the concentrations of the reactants exceed those of the products at equilibrium. Any reaction proceeds to a lesser extent from left to right, the smaller the value of the constant. The small value of the constant ($10^{-11.2}$) for the equilibrium considered in *Example 1* indicates that the reaction proceeds to the right only to an inappreciable extent. We may then conclude that the reaction has a pronounced tendency to proceed from right to left. In other words, it should be possible to precipitate copper from solutions of its salts by merely passing hydrogen gas into the solution. However, this reaction does not take place at ordinary temperatures because its speed is too slow. It should be possible to affect this change by means of a catalyst. This is not feasible with a contact catalyst since its surface would immediately become covered with metallic copper, rendering it inactive. But by increasing the temperature to 150° C the velocity of the reaction is increased sufficiently to bring about the reduction of cupric ion to free copper by hydrogen.

Example 2.

Let us determine the extent to which metallic copper dissolves in nitric acid solution to form cupric ion and nitric oxide. The equation for the reaction is

$$3Cu + 2NO_3^- + 8H^+ = 3Cu^{++} + 2NO + 4H_2O \tag{5}$$

Consequently,

$$\frac{(Cu^{++})^3(NO)^2H_2O^4}{Cu^3(NO_3^-)^2(H^+)^8} = \frac{(Cu^{++})^3(NO)^2}{(NO_3^-)^2(H^+)^8} = K_{eq} \qquad (6)$$

In equation (6) the equilibrium expression is written in two forms. In the first, solid *Cu* and H_2O are included but it is to be understood that they have no significance and are to be disregarded in that the concentration of H_2O does not change appreciably. They may be regarded as always being equal to 1. This is the same as eliminating them from the expression finally obtained.

The value for the half-reaction $\frac{(Cu^{++})^{\frac{1}{2}}}{Cu^{\frac{1}{2}}}$ is $10^{-5.6}$, for one electron change (see #59 of Table 27). For a change of two electrons the value is $10^{-11\,2}$, which when raised to the third power becomes $10^{-33\,6}$. The value for the half-reaction constant for $\frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8}$ is that for $\frac{(NO)^{\frac{1}{3}}H_2O^{\frac{2}{3}}}{(NO_3^-)^{\frac{1}{3}}(H^+)^{\frac{4}{3}}}$ (the inverse of #95 of the table) raised to the sixth power,

$$\frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8} = (10^{16\,2})^6 = 10^{97\,2}$$

Therefore

$$\frac{(Cu^{++})^3}{Cu^3} \times \frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8} = \frac{(Cu^{++})^3(NO)^2}{(NO_3^-)^2(H^+)^8} = 10^{-33\,6} \times 10^{97\,2} = 10^{63\,6} \qquad (7)$$

With such a high positive value as $10^{63\,6}$ it is evident that the reaction will take place. Experiment verifies this conclusion.

Example 3.

Is it possible for nitric acid to react with metallic zinc with the formation of zinc and ammonium ions? The balanced and completed equation for the reaction is

$$4Zn + NO_3^- + 10H^+ = 4Zn^{++} + NH_4^+ + 3H_2O \qquad (8)$$

The equilibrium expression is

$$\frac{(Zn^{++})^4}{Zn^4} \times \frac{(NH_4^+)H_2O^3}{(NO_3^-)(H^+)^{10}} = \frac{(Zn^{++})^4(NH_4^+)}{(NO_3^-)(H^+)^{10}} = K_{eq} \qquad (9)$$

The value for $\frac{(Zn^{++})^4}{Zn^4}$ for a two electron change taken to the fourth

power is $(10^{12.9})^8$ or 10^{103} (see #15 of Table 27), while the value for the half-reaction, $\frac{(NH_4^+)H_2O^3}{(NO_3^-)(H^+)^{10}}$ is $(10^{15.3})^8$ which is equal to 10^{122} (#92 of Table 27). Therefore the value for the equilibrium constant of equation (8) is $10^{103} \times 10^{122} = 10^{225}$. This value is so much greater than unity that the reaction readily proceeds and the equilibrium position is practically completely to the right. This does not mean that the ammonium ion is the only possible product. Calculation would show that other compounds with different valence states of nitrogen, such as NO and NO_2 can be formed by the action of nitric acid on zinc. Which of the nitrogen compounds are formed to the largest extent will depend upon the relative speeds of the different reactions involved.

Making the same calculation but using copper instead of zinc we find that the reaction which produces cupric and ammonium ions is likewise possible but the tendency for the reaction to proceed is not so great. The fact that ammonium ion is not found to a large extent when copper reacts with nitric acid must be attributed to the slow speed of this reaction as compared with the speed of those reactions which produce nitric oxide and nitrogen dioxide.

Example 4.

Table 27 may also be used in conjunction with the solubility product constants and with the ionization constants of weak acids and weak bases. *Examples 4 and 5* are designed to illustrate the use of this application.

Is it possible for nitric acid to dissolve an appreciable amount of cupric sulfide with the formation of nitric oxide, cupric ion and free sulfur? The equation for the reaction is

$$3CuS + 2NO_3^- + 8H^+ = 3S + 3Cu^{++} + 2NO + 4H_2O \qquad (10)$$

Therefore

$$\frac{(Cu^{++})^3(NO)^2H_2O^4S^3}{CuS^3(NO_3^-)^2(H^+)^8} = K_{eq} \qquad (11)$$

Since solid CuS is involved we must use the solubility product expression for CuS which is $(Cu^{++})(S^{--})$ or $\frac{(Cu^{++})(S^{--})}{CuS}$. This demands that a $(S^{--})^3$ appear in the numerator. Likewise, it is necessary to use the half-reaction expression $\frac{S}{(S^{--})}$ which in turn demands a

$(S^{--})^3$ in the denominator. To satisfy both these conditions multiply both numerator and denominator by $(S^{--})^3$.

$$\frac{(Cu^{++})^3(S^{--})^3}{CuS^3} \times \frac{S^3}{(S^{--})^3} \times \frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8} = K_{eq} \qquad (12)$$

Equation (10) involves a six electron change and the expressions (11) and (12) are likewise for a six electron change. Therefore all half-reaction constants must be raised to the sixth power. The solubility product constant for CuS is $10^{-35.4}$ (see Table in the Appendix).

$$\frac{(Cu^{++})^3(S^{--})^3}{CuS^3} = (10^{-35.4})^3 = 10^{-106}$$

$$\frac{S^3}{(S^{--})^3} = (10^{7.9})^6 = 10^{47.4} \text{ (\#19 of Table 27)}$$

$$\frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8} = (10^{16.2})^6 = 10^{97.2} \text{ (\#95 of Table 27)}$$

$$\frac{(Cu^{++})^3(S^{--})^3}{CuS^3} \cdot \frac{S^3}{(S^{--})^3} \cdot \frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8} =$$

$$10^{-106} \times 10^{47.4} \times 10^{97.2} = 10^{38.6} \qquad (13)$$

Omitting all solid phases and H_2O, we have

$$\frac{(NO)^2(Cu^{++})^3}{(NO_3^-)^2(H^+)^8} = 10^{38.6}$$

Consequently this reaction can proceed in accordance with equation (10). Experience in the laboratory verifies this conclusion.

Carrying out a similar calculation using mercuric sulfide instead of cupric sulfide we find that this substance has a relatively small tendency to be dissolved by nitric acid.

Example 5.

Is it possible for a solution containing 0.1 mole of acetic acid and 0.1 mole of sodium nitrate per liter to dissolve cadmium sulfide appreciably? The equation for the reaction is

$$3CdS + 2NO_3^- + 8HAc = 3Cd^{++} + 3S + 2NO + 8Ac^- + 4H_2O \qquad (14)$$

and the corresponding equilibrium expression,

$$\frac{(Cd^{++})^3(NO)^2(Ac^-)^8H_2O^4S^3}{CdS^3(NO_3^-)^2(HAc)^8} = K_{eq} \qquad (15)$$

Multiplying the numerator and the denominator of this expression by $(S^{--})^3 \times (H^+)^8$, we obtain

$$\frac{(Cd^{++})^3(S^{--})^3}{CdS^3} \cdot \frac{S^3}{(S^{--})^3} \cdot \frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8} \cdot \frac{(H^+)^8(Ac^-)^8}{(HAc)^8} = K_{eq} \quad (16)$$

$$\frac{(Cd^{++})^3(S^{--})^3}{CdS^3} = (10^{-26\,2})^3 = 10^{-78\,6} \text{ (from solubility product constant)}$$

$$\frac{(NO)^2H_2O^4}{(NO_3^-)^2(H^+)^8} = 10^{16\,2})^6 = 10^{97\,2} \text{ (\#95 of Table 27)}$$

$$\frac{S^3}{(S^{--})^3} = (10^{7\,9})^6 = 10^{47\,4} \text{ (\#19 of Table 27)}$$

$$\frac{(H^+)^8(Ac^-)^8}{(HAc)^8} = (10^{-4\,7})^8 \cong 10^{-37} \text{ (from the ionization constant for acetic acid)}$$

The value of the above expression then becomes

$$10^{-78\,6} \times 10^{97\,2} \times 10^{47\,4} \times 10^{-37} \quad \text{or} \quad 10^{29}$$

Therefore $\frac{(Cd^{++})^3(NO)^2(Ac^-)^8}{(NO_3^-)^2(HAc)^8} = 10^{29}$. If the (NO_3^-) and (HAc) were each 0.1 mole (i.e., 10^{-1} mole) per liter, the denominator becomes 10^{-10} and the numerator then has a value of 10^{19}. If the (Ac^-) should reach a value of 0.1 mole per liter as a maximum and the (NO) a pressure of one atmosphere (since it is a gas), $(Cd^{++})^3$ would be $10^{19}/10^{-8}$ or 10^{27} at equilibrium. Therefore cadmium sulfide would readily dissolve in this solution to form free sulfur and cadmium ion provided, of course, that the rate of the reaction is sufficiently great. The values given above merely show that such a reaction is possible and that there is a pronounced tendency for it to take place, but they give no information concerning the speed of the reaction.

Carrying out a similar calculation using cupric sulfide instead of cadmium sulfide, we find that the above solution will not dissolve the cupric sulfide appreciably.

Restrictions in the Interpretation of Results of Calculations. The calculations made from the foregoing table only show what the equilibrium will be when it is attained, but they do not indicate in any way that the equilibrium will be

attained in a reasonable period of time. The time necessary to reach equilibrium will depend upon the speed of the reaction. The velocity of a reaction is a factor which is independent of the equilibrium. If, however, calculation shows that a reaction cannot take place because of equilibrium restrictions, then the velocity of the reaction does not become a consideration, for no reaction can proceed beyond its equilibrium value. In other words, calculations from Table 27 show definitely when a reaction *does not take place* to any appreciable extent and show which reactions *will take place* only if the velocity is great enough.

Often several different products can be formed from the same reactants. For example, zinc reacting with nitric acid produces NO, NO_2 or NH_4^+ ion. The relative amounts of these substances formed will depend upon the relative velocities of the respective reactions involved.

Do Reactions Take Place Completely? If a reaction takes place completely its equilibrium constant must be equal to infinity. Strictly speaking, no reaction goes to completion but many reactions have such large values for their equilibrium constants that for all practical purposes we may regard them as complete. For example, the reaction

$$5H_2S + 2MnO_4^- + 6H^+ = 2Mn^{++} + 5S + 8H_2O \qquad (20)$$

has an equilibrium constant equal to 10^{232}. Such a large value of this constant is practically equivalent to complete reaction. Likewise, the equilibrium constant for the reaction

$$3H_2S + Cr_2O_7^{--} + 8H^+ = 2Cr^{+++} + 3S + 7H_2O \qquad (21)$$

is 10^{121}. It is not entirely meaningless to use such large numerical values. These two values show that MnO_4^- ion, in the presence of H^+ ion, is a better oxidizing agent than is $Cr_2O_7^{--}$ ion in the same medium, and that it is even possible for MnO_4^- ion with H^+ ion to oxidize Cr^{+++} ion to $Cr_2O_7^{--}$ ion.

Problems and Exercises

1. Calculate the equilibrium constant for each of the following oxidation-reduction reactions. In each case determine whether it is

possible for the reaction to proceed from left to right to any appreciable extent.

	Equation for Reaction	*Ref. Nos. in Table 27* *
(a)	$2Fe^{+++}+H_2SO_3+H_2O=SO_4^{--}+2Fe^{++}+4H^+$	49, 86
(b)	$2H_2S+H_2SO_3=3S_{(s)}+3H_2O$	44, 67
(c)	$3Cl^-+2NO_3^-+5H^+=3HClO+2NO+H_2O$	95, 107, 117
(d)	$3MnO_4^{--}+2H_2O=MnO_{2(s)}+2MnO_4^-+4OH^-$	75, 78
(e)	$2Cr^{+++}+6Co^{+++}+7H_2O=Cr_2O_7^{--}+6Co^{++}+14H^+$	106, 124
(f)	$3ZnS_{(s)}+2NO_3^-+8H^+=3Zn^{++}+3S_{(s)}+2NO+4H_2O$	19, 95
(g)	$4ZnS_{(s)}+NO_3^-+10H^+=4Zn^{++}+4S_{(s)}+NH_4^++3H_2O$	19, 92
(h)	$CdS_{(s)}+SO_4^{--}+4H^+=Cd^{++}+S_{(s)}+H_2SO_3+H_2O$	19, 49
(i)	$Br^-+MnO_{2(s)}+3H^+=HBrO+Mn^{++}+H_2O$	97, 102, 115
(j)	$CuS_{(s)}+SO_4^{--}+4H^+=Cu^{++}+S_{(s)}+H_2SO_3+H_2O$	19, 49
(k)	$Cu_{(s)}+2HNO_2+2H^+=Cu^{++}+2NO+2H_2O$	59, 96
(l)	$PbS_{(s)}+4H_2O_2=PbSO_{4(s)}+4H_2O$	19, 49, 67, 123
(m)	$Sn^{++}+H_2O_2+2H^+=Sn^{++++}+2H_2O$	45, 123
(n)	$CoS_{(s)}+2NO_3^-+4H^+=Co^{++}+N_2O_4+S_{(s)}+2H_2O$	19, 89
(o)	$10Br^-+2MnO_4^-+16H^+=2Mn^{++}+5Br_2+8H_2O$	97, 113
(p)	$H_3AsO_4+2I^-+2H^+=I_2+HAsO_2+2H_2O$	72, 74

2. Is it possible for metallic tin to be dissolved appreciably by nitric acid to produce Sn^{++} ion and NH_4^+ ion?
3. Is it possible for mercuric sulfide to be dissolved appreciably by nitric acid with the production of Hg^{++} ion, nitric oxide, and free sulfur?
4. A solution is 0.1 molar with respect to each of $Cr_2O_7^{--}$, H^+, and Cl^- ions. Can a reaction proceed to an appreciable extent in this solution to form free chlorine and Cr^{+++} ion?
5. Can cupric sulfide be dissolved to any appreciable extent by a solution containing hydrogen peroxide and hydrochloric acid to form Cu^{++} ion, free sulfur, and water?
6. Can silver sulfide be dissolved to any appreciable extent by concentrated nitric acid with the formation of Ag^+ ion, free sulfur, and nitric oxide?

* In addition to the half-reaction constants, the solubility product constants for slightly soluble substances are also required for several of these calculations.

7. From the half-reactions, Nos. 91, 107, and 117 in Table 27, calculate the ionization constant for hypochlorous acid, HClO.
8. From the half-reactions, Nos. 19 and 44 of Table 27, and K_W (water), calculate the value of the equilibrium constant for the reaction,

$$S^{--} + 2H_2O = S_{(s)} + 2OH^- + H_2$$

9. From half-reaction No. 44 and the first and second ionization constants for H_2S, determine the value of the constant for half-reaction No. 19, and compare your answer with that given in Table 27.
10. From the half-reaction No. 67, together with the first and second ionization constants for sulfurous acid and K_W, determine the value of the half-reaction, $S_{(s)} + 6OH^- \text{——} SO_3^{--} + 3H_2O$, i.e., for the expression

$$\frac{(SO_3^{--})^{\frac{1}{4}} H_2O^{\frac{3}{4}}}{S^{\frac{1}{4}}(OH^-)^{\frac{3}{2}}}$$

11. Using the result obtained in (10), together with half-reaction No. 19 and the solubility product constants for $Fe(OH)_3$, $Fe(OH)_2$, and FeS, determine whether the following reaction can proceed from left to right.

$$7Fe(OH)_{2(s)} + SO_3^{--} + 3H_2O = FeS_{(s)} + 6Fe(OH)_{3(s)} + 2OH^-$$

12. A solution containing Fe^{+++} ion is reduced with metallic iron. At equilibrium the concentration of the Fe^{++} ion is found to be .01 *M*. What is the concentration of the Fe^{+++} ion in this solution when it is in equilibrium with the Fe^{++} ion and metallic iron?

CHAPTER

14

Nuclear Chemistry

In the last two decades research chemists and physicists have given a great deal of attention to the study of the nucleus. The atomic or nuclear bomb and nuclear power are the direct result of these studies. Not only has the nucleus of the uranium atom been exhaustively studied but a great deal of research has been devoted to the nuclei of all the elements. Today there is such a wealth of information in this field that it has been classified as a new branch of chemistry. This branch has to do with the reactions of the nuclei and the fundamental particles such as the neutron and the proton. Such reactions are known to take place in the hot stars. They can be studied in the laboratory only by the use of high voltage machines such as the cyclotron which have the ability to impart high velocities, i.e., large kinetic energies, to the electrically charged particles.

The products of nuclear reactions very often are radioactive, and are used as a convenient and rapid means of analysis. The study of this radioactivity is often referred to as radiochemistry. It is a branch of the general field of nuclear chemistry.

The Neutron and the Structure of the Nucleus. In 1932 the English physicist, Chadwick, discovered a new fundamental particle, the neutron. This discovery was of the greatest importance to the study of the nucleus. It changed our concept of nuclear structure and brought about a tremendous

advance in the study of nuclear reactions — one of these reactions being the fission reaction of uranium in the atomic bomb and in the nuclear power reactor.

The neutron has a mass of 1.00893, while the mass of the proton is 1.008123 — their masses are very nearly alike. (These values are based upon the weight of the oxygen atom as a standard. This is taken to be 16.00000.) The size or cross section of the neutron is very small as compared with that of an atom — it is of the same order of magnitude as the nucleus of the hydrogen atom; i.e., the proton. It has no charge; therefore it is not repelled nor is it attracted by the positively charged nuclei or by the negatively charged electrons that make up the atom. Consequently, neutrons travel relatively great distances through matter without collision or reaction, and, therefore, neutrons cannot be contained in a bottle, or in any container, as can the atoms and molecules of ordinary matter. Many neutrons, produced by cosmic rays, pass through the human body every second.

The average time that a free neutron lives is about 15 minutes. At the end of this time it decomposes into a proton and an electron.

$$\begin{aligned} &\text{Neutron} \rightarrow \text{proton} + \text{electron} \\ &\text{or } n \rightarrow p + e^- \end{aligned} \tag{1}$$

However, this instability applies only to free neutrons and not to those combined in the nucleus.

Previous to the discovery of the neutron, the nucleus was assumed to be composed of protons (the nuclei of hydrogen atoms) and electrons. Thus the nucleus of the nitrogen atom with an atomic weight of 14 was assumed to be composed of 14 protons and 7 electrons (the weight of the electrons is negligible). This combination would account for an atomic weight of 14 and a charge on the nucleus of plus 7. However, we now assume that the nucleus of the nitrogen atom is composed of 7 protons and 7 neutrons. There is an experimental basis for this new concept, which is roughly the following. The nucleus as well as the atom is quantized, and the outer electrons

are coupled with the nucleus. From the quantized characteristics of the whole atom it is possible to determine whether there is an even or odd number of fundamental particles making up the nucleus. In the case of the nitrogen atom it is found that the nucleus is made up of an even number of fundamental particles. Hence the concept that it is made up of 14 protons plus 7 electrons is ruled out for 14 + 7 is an odd number whereas 7 protons plus 7 neutrons gives an even number. This rule applies to all nuclear species that have even atomic weights and an odd number of positive charges (i.e., odd atomic numbers).

Isotopes. The mass spectrograph is an instrument which, by means of a combination of electric and magnetic fields, has the ability to separate and distinguish particles with different e/m ratios (e is the electric charge on the particle and m is its mass). Thus, if singly charged atoms (not nuclei) of O^+ and N^+ (produced by removing one electron from the atom) are analyzed by this instrument it is found that the ratio of the two masses is 16 to 14. By means of this instrument it was found, for example, that not all oxygen atoms found in nature have the same mass. Three species were found. Those with a mass of 16 constituted the greater part of the "mass spectrum." The other two species have masses of 17 and 18, respectively. These different species are called **isotopes.** An isotope is a member of a group or family of atoms which have the same nuclear charge or atomic number; therefore, the same number of outer electrons. The relative amounts of these different oxygen isotopes present in our universe, or at least on our planet, are: ${}_8O^{16}$, 99.76 percent; ${}_8O^{17}$, 0.04 percent; ${}_8O^{18}$, 0.20 percent. In the designation ${}_8O^{16}$, as an example, the left-hand subscript refers to the atomic number and the right-hand superscript to the mass number, i.e., the total number of protons and neutrons. The nucleus of the ${}_8O^{16}$ isotope is made up of 8 protons and 8 neutrons; that of ${}_8O^{17}$, 8 protons and 9 neutrons; and for ${}_8O^{18}$, 8 protons and 10 neutrons.

The gross chemical properties of these different isotopes are the same, for the charges on the nuclei are the same — plus

8, in the case of oxygen, and therefore the number of external electrons — is the same in each case. All elements with the exception of about twenty, are characterized by two or more isotopes. Some of the most interesting isotopes, together with their exact masses, are given in Table 28.

TABLE 28

THE PROPERTIES OF ISOTOPES OF SOME OF THE ELEMENTS

Atomic Number	Element	Mass Number	Isotopic Weight	Packing Fraction
0	Neutron	1	1.0893	+89.3
1	Hydrogen	1	1.0081	+81
1	Deuterium	2	2.0147	+23
1	Tritium	3	3.0171	+57
2	Helium	3	3.0171	+57
2	Helium	4	4.0039	+ 9.8
3	Lithium	6	6.0167	+27.8
3	Lithium	7	7.0180	+25.7
4	Beryllium	8	8.0078	+ 9.8
4	Beryllium	9	9.0149	+16.6
4	Beryllium	10	10.0164	+16.4
5	Boron	10	10.0161	+16.1
5	Boron	11	11.0128	+11.6
6	Carbon	12	12.0036	+ 3.0
6	Carbon	13	13.0073	+ 5.6
7	Nitrogen	14	14.0073	+ 5.2
7	Nitrogen	15	15.0048	+ 3.2
8	Oxygen	16	16.0000	0
90	Thorium	232	232.020	+ 3.0
92	Uranium	235	235.084	+ 3.6
92	Uranium	238	238.088	+ 3.7

The Stability of the Isotopes. When we speak of the stability or instability of any substance we must always have in mind some change, — i.e., some chemical reaction. When we say that TNT (trinitrotoluol) is unstable, we mean that it is unstable with respect to its usual dissociation products that

result from explosion; namely, CO, CO_2, NO, NO_2, and H_2O. In saying that TNT is unstable with respect to its dissociation products we mean that when TNT explodes it releases energy. This release of energy is a measure of its instability.

There is another distinctly separate factor that must be considered when we consider the stability of any molecule or mixture of molecules. That is the velocity of the reaction. A mixture of gasoline and oxygen is unstable, for, if a reaction were to take place, energy would be released. Yet a sealed flask containing these substances could be kept indefinitely at room temperature without explosion occurring. Likewise TNT, while unstable, must be triggered off by a detonator, or by a percussion cap. The N_2, O_2, and H_2O in our atmosphere are unstable with respect to nitric acid. In other words, if the reaction were fast enough, these substances would combine to form nitric acid. There are, therefore, the two aspects of stability to consider: (1) the energy release if reaction takes place, and (2) the probability or the conditions under which the reaction can be made to proceed. Let us first consider stability in terms of the energy released, assuming the reaction can be made to take place.

Einstein deduced from his Theory of Relativity that mass and energy are related by the equation

$$E = mc^2 \tag{2}$$

where E is energy in ergs; m is mass in grams; and c is the velocity of light (3×10^{10} cm. per second). For any reaction the change in mass of all the atoms or molecules involved ($m_2 - m_1$) or Δm multiplied by c^2 equals the energy, $E_2 - E_1$ or ΔE, in ergs. In terms of change in mass and energy change, Einstein's equation is written as

$$\Delta E = c^2 \Delta m$$

When 12 grams of carbon combine with 32 grams of oxygen to form carbon dioxide, 96,000 calories or 3.94×10^{12} ergs of energy are released. The weight of the carbon dioxide formed does not exactly equal the weight of the carbon and the oxygen but is less than this amount by

$$\Delta m = \frac{\Delta E}{c^2} = \frac{3.94 \times 10^{12}}{9 \times 10^{20}} = 4.4 \times 10^{-9} \text{ gram}$$

This small difference in weight is much too small for us to weigh accurately. However, nuclear reactions are thousands of times more energetic than are ordinary chemical reactions, and this mass and energy relationship can be determined experimentally. Therefore the relative stabilities of the nuclei can be determined by their exact masses. The exact masses of

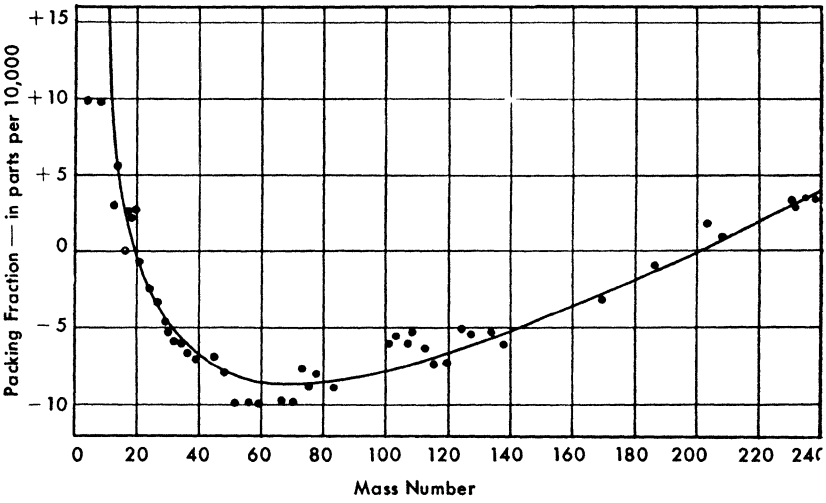


FIG. 14.1 The packing fraction of the isotopes as related to the mass number.

the various isotopes from which energy evolution can be calculated are given in Table 28.

The isotopic masses can be expressed in another way, i.e., by the "packing fraction." The packing fraction of the elements is also given in Figure 14.1. The relationship shown in this figure is very important for it is by means of these data that the potentialities of the A-bomb and atomic power were predicted.

The packing fraction is defined as the fractional deviation from the mass number. The packing fraction for helium can be determined in the following way. Since the mass of $_2He^4$ isotope is 4.0039, the packing fraction is

$$\frac{4.0039 - 4.0000}{4} = \frac{0.0039}{4} = 0.00097, \text{ or } 9.7 \times 10^{-4}.$$

The packing fraction is usually expressed as the number multiplied by 10^{-4}, or, in this case, +9.7. Another way of expressing this value is: the packing fraction of the $_2He^4$ isotope is plus 9.7 parts in 10,000.

Since, in changes of mass, we are not interested in the absolute mass but only in the changes, it does not make any difference what standard or what value we assume as the zero point — the difference will always be the same. So we arbitrarily assign to the mass of $_8O^{16}$ isotope the value of 16.0000. . . . The student will note that the packing fraction for O^{16} is zero.

As can be seen from Figure 14.1, some of the packing fractions have negative values. The packing fraction of $_{56}Ba^{138}$ is

$$\frac{137.916 - 138.000}{138} = \frac{-.084}{138} = -6.1 \times 10^{-4}, \text{ or } -6.1, \text{ as expressed}$$

in Figure 14.1.

When Otto Hahn, the German chemist, found that one of the dissociation products of U^{235} was barium, the tremendous potentialities and consequences of this discovery were realized by him and particularly by his colleague Lise Meitner. To better understand the Einstein equation relating mass and energy and to appreciate how the work of many contributes to our general knowledge of science, let us trace, as best we can, the thinking of Dr. Meitner, when she first learned that barium was one of the products found in the fission of U^{235}.

The reaction under consideration was

$$_{92}U^{235} + n \rightarrow {}_{56}Ba^{?} + {}_{36}Kr^{?} + ? \qquad (3)$$

It was assumed that only two atomic nuclei were formed. If Ba with an atomic number of 56 was one of these, then the other must be the element the atomic number of which is 92 − 56 = 36, or krypton. (This assumption was later confirmed by experiment.) But it was apparent that in this reaction there were too many neutrons. These were spilled over, so to speak. It was this deduction that led to the idea

of the chain reaction and to the great possibility of the A-bomb and atomic power. The other factor in Dr. Meitner's consideration was the energies involved. To follow her reasoning further, let us now calculate the energy released when U^{235}, reacting with a neutron, dissociates into barium and krypton. To do this, we shall consider only the average line — the solid line — of Figure 14.1, and, therefore, make a very rough calculation. The packing fraction of uranium is +3.6; that of barium is about −6; and that for krypton is about −8. The average packing fraction for the products of the reaction is $\frac{(-6)+(-8)}{2}$ $= -7$. So the difference in packing fraction between ${}_{92}U^{235}$ and its products is roughly $+3.7-(-7) = 10.7$. The difference, 10.7, means that in the reaction involving one gram atom of U^{235} the mass has decreased $\frac{10.7}{10{,}000} \times 235$ or 0.25 gram. According to equation (2) this mass change is equal to 2.5×10^{-1} grams $\times 9 \times 10^{20}$ cm $= 2.2 \times 10^{20}$ ergs. This value is equivalent to about 220 Mev (million electron volts). Within our rough calculations this checks with the experimentally determined energy release. This is an added confirmation of equation (2). One gram of TNT upon explosion releases about 4×10^{10} ergs. So one gram atom of U^{235} if every atom underwent fission, would yield the equivalent of $\frac{2.2 \times 10^{20}}{4 \times 10^{10}} = 5.5 \times 10^{9}$, grams, or about 5,000 tons of TNT. The A-bombs exploded in World War II were rated at 20,000 tons of TNT or equivalent to about 1 kilogram (2.2 pounds) of exploding U^{235}. Of course, the efficiency of exploding the U^{235} was not 100 percent, so a greater amount than this was used. Later we shall use Table 28 to consider the energies possible with an H-bomb.

Radioactivity. The "mass defect" or the packing fraction forms one criterion of the stability of the nucleus. Another criterion is that involving the "decay" of the most unstable of the isotopes.

In 1896, long before we were able to make artificial radioactive isotopes in the laboratory, Becquerel, a French physicist,

discovered radioactivity in uranium ores. His first results showed that uranium ores and particularly uranium salts had the property of blackening a photographic plate, even though the photographic plate was protected by an ordinary wrapper against light. In 1898, Pierre and Marie Curie began their experiments of isolating the radioactive substance which was contained in these ores. It was found to be radium.

Later it was shown that radioactivity could be ascribed to other elements related in a way to uranium and thorium, and that it manifested itself in three ways. In terms of knowledge gained later, these three processes involve the emission from the nuclei of radioactive elements of (1) *alpha* particles (the nuclei of helium atoms, ${}_2He^4$); (2) *beta* particles (electrons); and (3) *gamma* rays or short X-rays (electromagnetic waves of very high frequency, i.e., high energy quanta). It was found, for example, that uranium 234 "decayed" into thorium 230 by emitting an *alpha* particle:

$$ {}_{92}U^{234} \rightarrow {}_{90}Th^{230} + {}_2He^4 \qquad (4) $$

Note that the subscripts (+ charges) and superscripts (mass numbers) must balance in an equation of this kind. Thorium 230 (or ionium) then decays into radium 226 by the emission of another *alpha* particle:

$$ {}_{90}Th^{230} \rightarrow {}_{88}Ra^{226} + {}_2He^4 \qquad (5) $$

This process of decay continues but not always with the emission of an *alpha* particle. In some cases *beta* particles or electrons are emitted from the nucleus. When an *alpha* particle is emitted, the nucleus loses 2 plus charges and therefore the outer electronic shell must rearrange in order to lose two electrons. Likewise when the nucleus loses an electron it gains one positive charge and an additional electron must be added to the electronic structure. From these radioactive observations it seems clear that the *alpha* particles, ${}_2He^4$, are particularly stable.

From our more modern concept of the structure of the nucleus we must conclude that the emission of a *beta* particle involves the disruption of a nuclear neutron

$$n \text{ (nuclear)} \rightarrow p \text{ (nuclear)} + e^-$$

The emission of *gamma* rays usually accompanies the emission of either *alpha* or *beta* particles. The final stable product of disintegration of uranium and thorium is lead, ${}_{82}Pb^{206}$, ${}_{82}Pb^{207}$ and ${}_{82}Pb^{208}$. It should be noted that the naturally occurring radioactive, and therefore unstable, isotopes are among the heaviest elements known.

The rate of decay of these isotopes varies greatly. In general, the greater the instability, as measured by the kinetic energy of the emitted particles, the faster is the rate of decay. The rate of decay, i.e., the rate of nuclear reaction, is measured in terms of "half life." The half life of any isotope is the period which is necessary for the number of the existing particles of the species to be reduced to one-half. The half life of ${}_{92}U^{235}$ is 7×10^8 or 700,000,000 years. This means that after a lapse of 7×10^8 years one-half of the ${}_{92}U^{235}$ atoms originally present are still in existence. After another 7×10^8 years one-half of the second batch are still "alive." In other words, after $2 \times 7 \times 10^8$ years, $\frac{1}{2} \times \frac{1}{2}$ or $\frac{1}{4}$ of the original amount are still existent. One-half of any number present will decay in 7×10^8 years regardless of past history.

The half lives of some examples of the naturally occurring radioactive isotopes are:

${}_{92}U^{235}$	7.07×10^8 years
${}_{88}Ra^{226}$	1590 years
${}_{92}U^{238}$	4.5×10^9 years
${}_{86}Rn^{222}$	3.825 days
${}_{84}Po^{218}$	3.05 minutes
${}_{84}Po^{214}$	1.5×10^{-4} seconds

In the above illustrations it must be apparent that the short lived isotopes cannot be present in any appreciable quantities in nature. Their properties must be caught "on the fly" in the laboratory.

While most of the naturally occurring radioactive elements are present among the heaviest elements known, there are a few among those with lower mass numbers; notably K^{40} with

a half life of 4.5×10^{10} years and Rb^{87} with a half life of 6×10^{10} years.

When the elements were first formed undoubtedly a large number of them had radioactive isotopes, but these have decayed into the stable non-radioactive isotopes now present on earth.

Today it is possible to produce a great number of different kinds of isotopes by irradiating the non-radioactive isotopes with neutrons in our atomic piles or nuclear reactors For example, ${}_{27}Co^{60}$ can be readily produced by irradiating ${}_{27}Co^{59}$ with neutrons. Cobalt-60 is a very active emitter of high energy *gamma* rays but it also emits *beta* rays with a half life of 5.3 years. As a result, it is today replacing radium for therapeutic purposes. The reaction for the formation of Co^{60} is

$$ {}_{27}Co^{59} + n = {}_{27}Co^{60} + \gamma \text{ (}gamma\text{ rays)} \tag{6} $$

Equation (6) can be written in the abbreviated form

$$ Co^{59}\ (n, \gamma)\ Co^{60} \tag{7} $$

The decay reaction is

$$ {}_{27}Co^{60} \rightarrow {}_{28}Ni^{60} + \beta^- \text{ (beta particle)} + \gamma \tag{8} $$

A very useful isotope, Na^{24}, with a half life of 14.8 hours can be produced by the reaction

$$ {}_{11}Na^{23} + n = {}_{11}Na^{24} + \gamma \tag{9} $$

The decay reaction of Na^{24} is

$$ {}_{11}Na^{24} \rightarrow {}_{12}Mg^{24} + \beta^- + \gamma \tag{10} $$

By means of such reactions many useful isotopes are now produced by the Atomic Energy Commission and are available to science and industry for research, analytical, and medical purposes.

The Fission Reaction. The most important nuclear reaction of our time is that of the fission (splitting) of the U^{235} nucleus. Previous to Hahn's and Strassman's discovery of fission in 1939, the largest particle emitted by the nucleus was

the *alpha* particle with a mass number of 4. In the fission process the nucleus of the uranium atom breaks into two major parts with a sprinkling of extra neutrons. The fission reaction is

$$_{92}U^{235} + n \rightarrow A + B + xn \qquad (11)$$

A and B are related in that the sum of their charges must be equal to 92. There are more than twenty different ways in which $_{92}U^{235}$ can undergo fission. One of these has been mentioned already, i.e., U^{235} breaking up into barium and krypton. About 6 percent of all fissions of U^{235} result in the formation of barium and krypton. The others distribute themselves in accordance with the curve shown in Figure 14.2. The fission products are not usually the ordinary stable isotopes but are radioactive. However, the end products of decay of the fission products are stable isotopes.

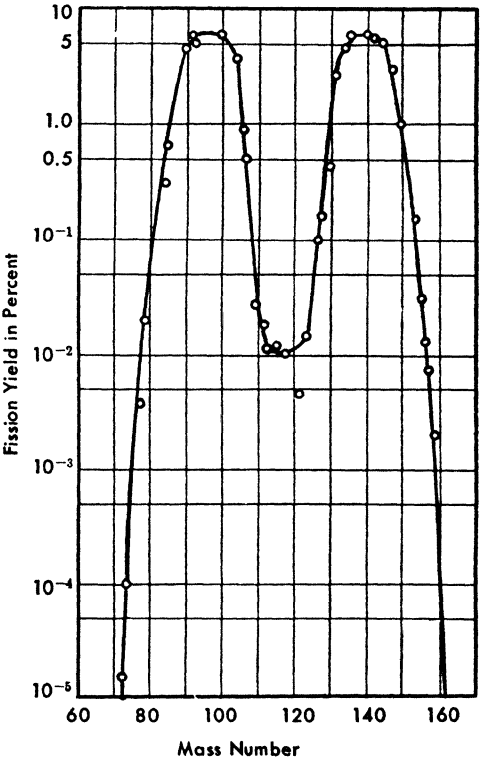


FIG. 14.2 The fission yield as related to mass number. The two peaks represent related ion pairs.

One can visualize the fission process in the following way. When the neutron enters the U^{235} nucleus it momentarily forms U^{236}. This nucleus is very unstable and undergoes vibrational motion just as a drop of water undergoes vibration when it is disturbed. This vibration gets so severe that, like the water droplet, it breaks into two parts but, in doing so, some minute droplets, neutrons, are splashed out. For every U^{235}

fission which takes place, about two and one-half neutrons, on the average, are splashed out. In the A-bomb and in the nuclear reactor these two and one-half neutrons serve as potential triggering particles for the fission of more U^{235} nuclei. These two and one-half neutrons could, under ideal conditions, produce $2.5 \times 2.5 \times 2.5$ or 15.6 neutrons, on the average and these in turn could trigger the fission of this same number

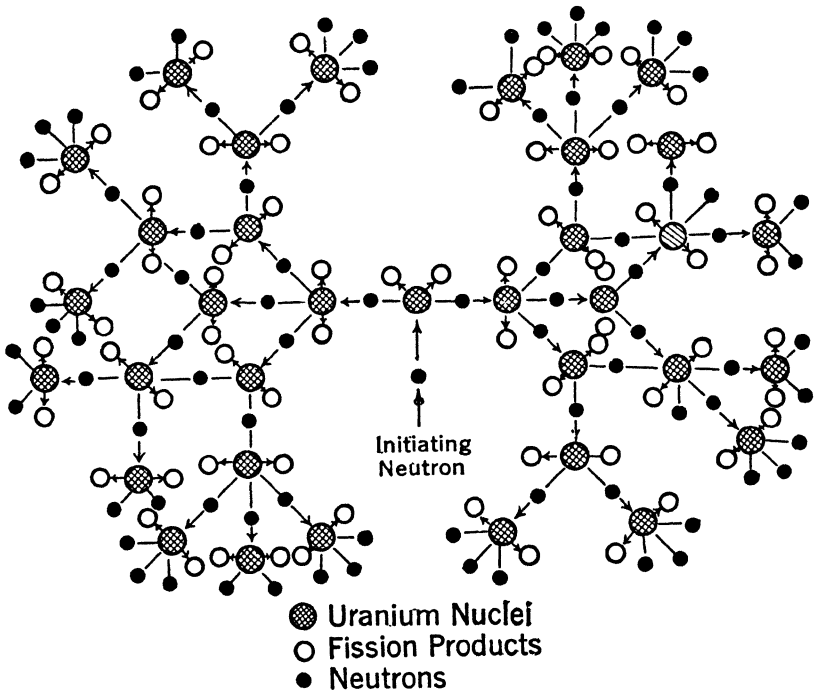


FIG. 14.3 The fission chain reaction.

U^{235} nuclei. Thus a chain reaction is set up, as shown schematically in Figure 14.3. In the A-bomb the whole reaction takes place in less than 10^{-6} (or one-millionth) second.

Transuranic Elements. Previous to World War II the heaviest element known was uranium, with an atomic number of 92. The heaviest element now known is Californium with an atomic number of 98.

Discoveries early in the war years led to the establishment of a huge plant for the production of plutonium-239, an

isotope which, like U^{235} is capable of neutron fission. $_{94}Pu^{239}$ is produced by the following reactions:

$$_{92}U^{238} + n \rightarrow {}_{92}U^{239} \tag{12}$$

$$_{92}U^{239} \rightarrow {}_{93}Np^{239} + \beta^- \text{ (23 minutes half life)} \tag{13}$$

$$_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + \beta^- \text{ (2.3 days half life)} \tag{14}$$

Uranium-238 is converted into uranium-239; this decays to neptunium-239; which, in turn decays to plutonium-239. The neutrons are supplied by the fission of U-235 in accordance with equation (11). These reactions were all carried out in nuclear reactors. By the time the war ended two new elements were officially added to the periodic table, namely, neptunium and plutonium. Since 1946, four more transuranic elements have been produced by Professor G. T. Seaborg and his collaborators at the University of California. These elements are americium, curium, berkelium, and californium, with atomic numbers of 95, 96, 97, and 98, respectively. They are all radioactive.

Fusion Reactions. These reactions involve the reactions between two light nuclei. Because of the electrostatic repulsions between nuclei, these reactions can only take place when the kinetic energies of the two nuclei, with respect to each other, are so great that penetration of one into the other is possible. At low relative velocities the two colliding nuclei repel each other and are deflected apart. Fusion, as well as fission, reactions can be made to take place in the laboratory by accelerating one nucleus by an electric field to a very high velocity and then directing it at a target which contains the nuclei to be bombarded. These reactions also take place in the hottest stars and in the heat center of an A-bomb. The temperature must be in the neighborhood of 100,000,000° C. Only the lightest nuclei can undergo such reactions, for with nuclei of greater charge the electrostatic repulsive forces become too great for the penetration of one nucleus into the other.

Let us calculate the energies evolved for a few of these reactions. In all cases we shall assume that the relative velocities

of the particles are great enough for penetration of the nuclei. The first reaction for consideration is that between two deuterons (deuterium nuclei) to produce $_2He^3$ and a neutron.

$$_1H^2 + {}_1H^2 \rightarrow {}_2He^3 + {}_0n^1 \qquad (15)$$

Referring to Table 28, we determine the sum of the masses of the members of the left-hand side of the equation and subtract the sum of the masses on the right-hand side.

Mass of two $_1H^2$	= 2×2.0147	= 4.0294
Mass of $_2He^3$	=	3.0171
Mass of n	=	1.0090
Difference	=	0.0033

Therefore, when about 4 grams of deuterium react, according to equation (15), the loss in mass is 0.0033 grams. If one kilogram of this substance reacts, then the loss in weight is

$$\frac{1000}{4} \times 0.0033 = 0.825 \text{ gram.}$$

Using the Einstein relationship that $\Delta E = \Delta m \times c^2$.

$$\Delta E = 0.825 \times 9 \times 10^{20} \text{ gram cm.}^2 \text{ sec.}^{-2}$$
$$= 7.4 \times 10^{20} \text{ ergs.}$$

Let us compare this energy release with TNT. One gram of TNT, on exploding, releases 4×10^{10} ergs. So one kilogram (about 2.2 pounds) of deuterium reacting in the above fashion releases a TNT equivalent of $\frac{7.4 \times 10^{20}}{4 \times 10^{10}}$ or 1.85×10^{10} grams — 1.85×10^7 kilograms, or 1.85×10^4 metric tons, or about 20,000 tons of TNT. This is about the same amount of energy released by 1 kilogram of U^{235} upon fission.

Another possible fusion reaction to consider is that between tritium $_1H^3$, and deuterium, $_1H^2$, nuclei. The reaction is

$$_1H^3 + {}_1H^2 \rightarrow {}_2He^4 + {}_0n^1 \qquad (16)$$

The sum of the masses on the left-hand side of the "equation" is 2.0147 + 3.0171 = 5.0318. The sum of the masses on the right side is 4.0039 + 1.0090 = 5.0129. The difference

in mass, i.e., the mass lost in the reaction, is 5.0318 – 5.0129 = .0189 gram. For 2 grams of ${}_1H^2$ plus 3 grams of ${}_1H^3$, the loss in mass is 0.0189 grams. For one kilogram of the mixture (400 grams of ${}_1H^2$ and 600 grams of ${}_1H^3$), the loss in mass, upon reaction, is $\frac{1000}{5} \times 0.0189 = 3.78$ gm. Pound for pound this is about four and one-half times the energy released by the fission of U^{235}.

These are some of the reactions that probably take place in the explosion of the H-bomb. A very high temperature is necessary to initiate these reactions. The explosion of an A-bomb is one means for providing this temperature.

Applications of Radioactive Isotopes to Analysis. The radioactive isotopes differ from the non-radioactive isotopes of a given element in that the nuclei are different. The outer electronic structures of the different isotopes are the same and hence the chemical reactions are the same. However, the radioactive atoms differ in that they emit radioactive particles upon decay. Radioactive isotopes can then be used as tracers to follow the course of a reaction and, in fact, to make analytical determinations of a particular element. They are used in a great variety of ways in scientific research work. The following are only a very few examples.

Suppose we should like to determine the solubility of FeS in a very dilute acid solution. We would first add a known amount of radioactive iron atoms to a relatively large amount of non-radioactive iron atoms. (Suppose that one iron atom in every million is radioactive.) We would then convert the iron atoms to FeS. The FeS would then be placed in the dilute acid solution and equilibrium attained by shaking the mixture for a long time. The undissolved FeS then would be filtered off and the solution tested for its radioactivity by means of a Geiger counter. From the intensity of the gamma radiation emitted, the amount of FeS that had dissolved can be calculated.

Again, suppose we wish to determine the amount of iron in blood by the tracer technique. One procedure for carrying out

this analysis is as follows. A known amount of a radioactive iron salt is added to the drawn blood. The blood solution is then dried and ignited to burn away all the organic matter. Through the appropriate chemical reactions the iron (not necessarily all of it) is converted into relatively pure Fe_2O_3 and weighed. The radioactivity of the Fe_2O_3 is also determined. Since we know how much radioactive iron was added to the solution we can determine the total iron in the blood. To illustrate: suppose that the iron added to the blood contained one radioactive atom out of every hundred iron atoms and suppose we add 0.1 mg. of this tracer. Suppose further that the Fe_2O_3 formed was found to contain one atom of radioactive iron for every 10,000 iron atoms. We then know that the tracer solution had been diluted 100 times; i.e., there was 100 times as much iron in the blood as was added. Therefore the amount of iron in the blood sample would be 100×0.1 mg. or 10 mg.

Suppose that the inner wall of the cylinder of an automobile engine is made radioactive. The wear of the cylinder wall upon running the engine can be readily determined by measuring the radioactivity found in the lubricating oil after different periods of time. This technique can measure the loss of one-millionth of an inch from the cylinder wall and it is, therefore, a very rapid method as compared with an old technique of running the engine hundreds of hours, tearing it down, and measuring the diameter of the bore.

The most useful of all the tracers is carbon-14; or ${}_6C^{14}$, with a half-life of about 5,700 years. This isotope is now produced and distributed in the form of various compounds by the Atomic Energy Commission in relatively large quantities. The formation reaction is

$$ {}_7N^{14} + {}_0n^1 \rightarrow {}_6C^{14} + {}_1H^1 \qquad (17) $$

The decay reaction is ${}_6C^{14} \rightarrow {}_7N^{14} + \beta^-$. By making biological compounds of this tracer it is possible to determine many of the reactions which take place in the life processes of plants and animals.

Radiocarbon Dating. The cosmic rays, that originate in interstellar space and penetrate the earth's atmosphere, collide with matter in the atmosphere and produce neutrons. It has been shown that the number of such neutrons that reach the earth's surface is approximately one per second for each square centimeter of area. These neutrons encounter nitrogen atoms of the atmosphere (the atmosphere is composed of approximately 80 percent nitrogen) and, as a result, carbon-14 is produced in accordance with equation (17). This carbon combines with the oxygen of the atmosphere (20 percent composition) to form carbon dioxide containing radioactive carbon-14 nuclei having a half-life of about 5700 years. Carbon dioxide of the atmosphere is absorbed by plants to form starches and sugars with the liberation of oxygen. All animal life consumes plants for food; furthermore, the human race not only consumes plants but meat from animals as well. In other words, there exists in the plant and animal kingdoms an equilibrium as far as carbon-14 is concerned. It is produced as fast as it disappears by radioactive decay.

When any part of the plant or animal kingdom is removed from the equilibrium cycle, either by death or by its inaccessibility to carbon dioxide (containing radioactive carbon) necessary for growth, the carbon-14 present decays with a half-life of about 5700 years. By measuring the carbon-14 content of ancient materials, that have been removed from the equilibrium cycle, it is readily possible to determine the age of the materials. The material may be the cloth wrapping of an Egyptian mummy, the wood of an ancient redwood, the wood buried in a glacier of the last ice age, or the hemp of sandals found in caves used by early western habitation in the United States.

It is evident that carbon-14 may be used as a tracer to determine the age of many objects of archaeological interest, as they refer to ancient peoples, the last ice age, and to ancient civilizations. Professor W. F. Libby of the University of Chicago has developed and made use of this pro-

cedure to date hundreds of events of archaeological interest. He has been somewhat limited in the extent of his studies by the half-life of carbon-14. Twenty-thousand years is about the limit of time for dating since this is nearly four half-lives of carbon-14. Since 2^4 equals 16 and $\frac{1}{16}$ equals about 7 percent, it means that the decay of carbon-14 in 20,000 years takes place to the extent of 93 percent, and that only 7 percent of the radioactive carbon remains. It is very difficult indeed to measure the activity of any sample lower than this. One thousand years is about one-sixth of a half-life. Accordingly, it is very difficult to determine the age of samples less than 1000 years old. As a result, most of the reliable results fall in the age range of 1000 years to 20,000 years.

While radioactive tracers are not usually employed for routine analysis, they have already demonstrated their usefulness in scientific research.

The Age of the Earth and the Origin of the Elements. From the products of radioactive decay of some of the heavy radioactive elements occurring in minerals it is possible to determine the length of time that has lapsed since that mineral solidified. The radioactive elements which may be considered for this purpose are U^{238}, U^{235}, and Th^{232}. Each of these elements decays through a chain of radioactive reactions and the chain stops when lead is formed. The lead isotopes which are the end products of the decay reactions of the above named isotopes are Pb^{206}, Pb^{207}, and Pb^{208}, respectively.

Since we know the half lives of all the members of the chain then, if we can determine the relative amount of, e.g., U^{235}, and Pb^{207} in the same mineral, we can calculate the age of the mineral containing the radioactive isotopes. In making such determinations we must be sure that the mineral contains no naturally occurring lead. To ascertain this it is necessary to determine the amount of Pb^{204} present. This particular isotope does not result from radioactive decay. What is really determined is the ratio of Pb^{207} to Pb^{204}. Another factor the investigator must take into account is the

possibility that some of the lead has been leached out of the rock. He can check this by getting the ratio of the amounts of the isotopes Pb^{206} to Pb^{207}. One is the result of the decay of U^{238} and its "daughter" and the other comes from U^{235}.* Since the two chains do not decay at the same rate, this ratio may be used to calculate the age of the mineral. By these means the oldest age of various minerals has been determined to be between two and three billion years.

Another method is that of determining the helium and uranium contents of the minerals. Since the process of decay of the uranium isotopes, as well as the rates, is known, it is possible to determine the age of the mineral by analyzing the mineral for both uranium and the alpha particles which have become trapped as helium. In this case the assumption is made that none of the helium atoms have escaped. Obviously a small amount of helium will nevertheless escape so the value obtained by this method is a minimum one. The age of the crust of the earth and the age of meteorites has been determined by this method to be about two billion years.

These observations, together with the astronomical observations of the expanding universe, have led many scientists to seriously consider the hypothesis that our whole universe was formed in one gigantic explosion some three and one-half billion years ago. Astronomers have shown that all the stars and even other universes are receding from us at a very rapid rate. This rate is determined by the Doppler shift of the spectral lines. Everyone has noted the fact that the pitch of the whistle of a locomotive is lowered as it is going away from the listener. As the locomotive approaches the listener, the whistle is high-pitched, and as soon as it passes it abruptly changes to a low pitch. The lowering of the pitch is related to the ratio of the velocity of the locomotive to the velocity of sound. Likewise, a star moving away from us gives off a lower frequency of any one of the hydrogen lines than it would if it were stationary

* The student is advised to consult a text in general chemistry for a description of the decay processes of the three radioactive series originating with U^{238}, U^{235}, and Th^{232}, respectively.

with respect to the earth. By observations of this kind we find that all stars are moving outward. On the basis of these observations it has been calculated that all the stars, and even the other galaxies, began moving out from a region not too far from our solar system about three and one-half billion years ago.

One theory proposed by G. Gamow, an American astrophysicist, is that there once existed a great concentration of energy or mass (the two are equivalent; see equation 2), the dictionary name for which is ylem. It is defined as the primordial substance from which the elements are supposed to have been made. Perhaps in this explosion great quantities of neutrons were formed. The neutrons then decomposed into protons and electrons (half-life 15 minutes), and these then combined to form the nuclei and then the atoms. These nuclei were mostly radioactive and decayed into the present stable isotopes. Logical explanations of the formation and the distribution of our present elements can be made on this hypothesis.

This hypothesis is, of course, highly speculative. However, the two entirely different sets of data corroborate rather than deny such an hypothesis. Such an assumption nevertheless emphasizes the fact that there is much about nature that we do not yet know.

APPENDIX

Mathematical Operations

In designing the problems for this course, simplicity of mathematical operations has been one of the chief objectives. Since the primary purpose of these problems is the development of an understanding of chemical equilibrium, difficulties with mathematics would tend to impair the progress of the student. There are, however, a few simple mathematical operations, notations and concepts with which it is impossible to dispense. These are given in the nature of a review since it is assumed that the student is familiar with the simplest algebra and the use of logarithms.

The Use of Exponents. The small size and the large numbers of molecules with which we have to deal make it necessary to use numbers that are often beyond everyday range of thought. For example, there are 606,000,000,000,000,000,000,000 molecules in 1 mole or 1 gram molecule of any substance. Instead of expressing the number in this manner we use an abbreviated form, 6.06×10^{23} (6.06 times ten to the twenty-third power). The factor 10^{23} is equivalent to moving the decimal point twenty-three places to the right in the number 6.06. The number 2000 may be written 2×10^3, that is, 2×1000, for 10^3 is the product obtained when 10 is multiplied by itself 3 times; i.e., $10 \times 10 \times 10$. One million would be 10^6, and one billion, 10^9. The number 206,000 could be written in any one of the following ways:

0.206×10^6	206×10^3
2.06×10^5	2060×10^2
20.6×10^4	20600×10

The first, second, or third of these are obviously the most convenient.

Numbers very much smaller than 1 are expressed in a similar manner. Two-millionths may be written .000002, but for convenience it is better to write it as 2×10^{-6} (2 times ten to

the minus sixth power). In order to convert the second form to the first it is necessary merely to move the decimal point six places to the left. It is the same as $2/10^6$, that is, two divided by one million. Again, this number could be written in any of the following forms:

2.0×10^{-6}	$.002 \times 10^{-3}$
0.2×10^{-5}	$.0002 \times 10^{-2}$
$.02 \times 10^{-4}$	$.00002 \times 10^{-1}$
	.000002

The first two of these forms are the most convenient. The number 10^{-6} is the same as $0.1 \times 0.1 \times 0.1 \times 0.1 \times 0.1 \times 0.1$.

The use of the exponential form greatly facilitates the multiplication and division of either large or small numbers. In multiplying two purely exponential numbers the exponents are added, and this algebraic sum is used as the exponent of the answer. Examples:

$$10^3 \times 10^3 = 10^6$$
$$10^3 \times 10^{-2} = 10$$
$$10^{23} \times 10^{-6} = 10^{17}$$

Multiplying 4×10^7 by 6×10^4 becomes 24×10^{11}, that is, $(4 \times 6) \times (10^{7+4})$. Likewise,

$$6000 \times 210 = 6 \times 10^3 \times 2.1 \times 10^2 = 12.6 \times 10^5$$
$$420 \times 0.000036 = 4.2 \times 10^2 \times 3.6 \times 10^{-5} = 15.12 \times 10^{-3}$$
$$.00012 \times .00007 = 1.2 \times 10^{-4} \times 7.0 \times 10^{-5} = 8.4 \times 10^{-9}.$$

The reverse operation is performed by dividing one number by another. For the purely exponential part of the number the exponent of the divisor is subtracted algebraically from that of the dividend and the algebraic difference is used as the exponent of the answer. Thus,

$$10^6 \text{ divided by } 10^2 = 10^4$$

Examples of division are:

(a) $$4 \times 10^4 \div 2 \times 10^2 = \frac{4 \times 10^4}{2 \times 10^2} = \left(\frac{4}{2}\right) \times \left(\frac{10^4}{10^2}\right)$$
$$= 2 \times 10^2$$

(b) $$4 \times 10^4 \div 8 \times 10^{-6} = \left(\frac{4}{8}\right) \times \left(\frac{10^4}{10^{-6}}\right) = 0.5 \times 10^{4-(-6)}$$
$$= 0.5 \times 10^{4+6} = 0.5 \times 10^{10}$$

(c) $$3.2 \times 10^{-5} \div 4 \times 10^{-9} = \left(\frac{3.2}{4}\right) \times \left(\frac{10^{-5}}{10^{-9}}\right) = 0.8 \times 10^{-5-(-9)}$$
$$= 0.8 \times 10^{-5+9} = 0.8 \times 10^4 = 8 \times 10^3$$

Since the squaring of any number is the operation of multiplying the number by itself, $(2 \times 10^5)^2$ becomes,

$$2 \times 10^5 \cdot 2 \times 10^5 \text{ or } 4 \times 10^{10}$$

In extracting a square root of a purely exponential number, the exponent is merely divided by two and used in the answer:

$$\sqrt{10^4} = 10^2$$

The square root of $4 \times 10^{-4} = \sqrt{4} \times \sqrt{10^{-4}} = 2 \times 10^{-2}$. It is essential that the exponent be an even number in order to simplify the procedure; if it should not be an even number it may be easily changed as shown in the following cases:

(a) $\sqrt{0.4 \times 10^5} = \sqrt{4 \times 10^4}$

(or $(4 \times 10^4)^{\frac{1}{2}}$) $= \sqrt{4} \times \sqrt{10^4} = 2 \times 10^2$

(b) $\sqrt{2.5 \times 10^{-9}} = \sqrt{25 \times 10^{-10}}$

(or $(25 \times 10^{-10})^{\frac{1}{2}}$) $= 5 \times 10^{-5}$

(c) $\sqrt{81 \times 10^6} = (81 \times 10^6)^{\frac{1}{2}} = 9 \times 10^3$

The exponent $\frac{1}{2}$ may be substituted for the usual square root sign. Thus $\sqrt{2}$ is the same as $2^{\frac{1}{2}}$, and $\sqrt{3 \times 10^2}$, the same as $(3 \times 10^2)^{\frac{1}{2}}$.

The Use of Logarithms and Exponential Numbers. The common logarithm of any number is the power to which the number 10 must be raised to equal that number. Thus the logarithm of 1000 is 3, that is, the number 10 must be raised to the third power to be equal to 1000. Examples:

Number	*Number expressed exponentially*	*Logarithm*
1000	10^3	3
100000	10^5	5
10	10^1	1
1	10^0	0*
.01	10^{-2}	−2
.00001	10^{-5}	−5

To what power must 10 be raised to equal 50? Obviously, the value of this exponent must be between 1 and 2, for 50 lies between 10, the common logarithm of which is 1, and 100, the common logarithm of which is 2. The logarithm of 50 is 1.6990, that is, $50 = 10^{1.6990}$. When the exponent of 10 is not a whole number, we cannot give it the same simple interpretation as was done in the previous section. For example, to move the decimal point 1.6990 places to the right has no meaning. Nevertheless, any number may be expressed entirely in the exponential form. Examples are:

Number	*Logarithm of number*	*Number expressed exponentially*
20	1.3010	$10^{1.3010}$
310	2.4914	$10^{2.4914}$
.013	−1.8861	$10^{-1.8861}$

What was stated previously regarding the multiplication of exponential numbers applies here; that is, for multiplication the exponents are added, and for division, the exponents are subtracted. Thus,

$$20 \times 310 = 10^{1.3010} \times 10^{2.4914} = 10^{3.7924} = 6200$$

(The logarithm of 6200 is 3.7924.)

The exponent in question may be found in logarithm tables provided for this purpose. Accordingly, the procedure used to obtain the product of any two or more numbers by the use of logarithms is as follows: The logarithms of the numbers are

* Any finite number raised to the zero power is equal to 1.

taken from the tables and added. This sum of logarithms is the logarithm of the product of the original numbers which again may be obtained from the tables. Thus, to multiply 20 by 310 we add the logarithms of these numbers, 1.3010 and 2.4914, which gives 3.7924. By referring to the logarithm tables we find that the number 6200 corresponds to the logarithm 3.7924.

Similarly, in the process of division, the logarithms are subtracted. In order to divide 6240 by 39 we first find the logarithms for these numbers, 3.7952 and 1.5911, respectively. Subtracting the second from the first we obtain 2.2041 which, by referring to the tables, we find corresponds to 160, the answer. Another example is: Divide 3913 by 13.*

Logarithm of 3913 = 3.5925
Logarithm of 13 = 1.1139
Logarithm answer = 2.4786

The answer is 301 since it is the number which corresponds to the logarithm whose value is 2.4786.

Every logarithm is made up of two parts, the characteristic and the mantissa. The characteristic is that part of the logarithm which lies to the left of the decimal point, and the mantissa that part to the right of it. If the logarithm of a number is 4.3060, the characteristic is 4 and the mantissa is .3060. Only the mantissa is found in the logarithm table since the characteristic merely depends upon the position of the decimal point. For example, the logarithm for 316 is found in the tables to be 4996, which is only the mantissa. The characteristic is one less than the number of digits in the number 316, that is, 3 −1 or 2. So the logarithm for the number 316 is 2.4996 (or .4496 + 2). It will be observed that the mantissae for the logarithms of the numbers 316, 31.6 and 3.16 are all the same; only the characteristics are different: 2, 1 and 0 respectively.

The significance of the mantissa and the characteristic can

* In actual practice it would not be practical to use logarithms for such a simple case.

perhaps be better understood from the following considerations. The number 316 may be written 3.16×10^2.

logarithm of (3.16×10^2) = logarithm of 3.16 + logarithm of 10^2
logarithm of (3.16×10^2) = .4996 (mantissa)+2 (characteristic)
or logarithm of 316 = 2.4996

The logarithm of any number less than 1 has a negative value and great care must be used in dealing with such logarithms to avoid mistakes and confusion. The logarithm of such a number may be obtained easily by the same procedure as that given above. For example, the logarithm of .00316 is obtained as follows:

$$.00316 = 3.16 \times 10^{-3}$$
$$\text{logarithm of } .00316 = \text{logarithm of } 3.16 + \text{logarithm of } 10^{-3}$$
$$= .4996 + (-3) = .4996 - 3 = -2.5004$$

The logarithm of any number less than 1 is usually not expressed entirely as a negative number. For example the logarithm of .00316 usually would not be expressed as −2.5004 but rather as .4996 − 3. The abbreviated form for this last expression is $\bar{3}.4996$ or 7.4996 − 10. The reason for adopting this usage is that in this form the mantissae are always added in the process of multiplication; only the characteristics have negative values.

The characteristic of the logarithm of a number less than 1 is equal in magnitude to *one more* than the number of zeros between the first significant figure and the decimal point, and has a negative value. Thus the characteristic of the logarithm of .0013 is − 3, and that of the logarithm of .00006 is − 5. The logarithm of .0013 is then .1139 − 3. (This would be equal to − 2.8861 but for convenience is written as $\bar{3}.1139$ or usually 7.1139 − 10.)

Examples:

	Number	*Logarithm*
(a)	.0167	8.2227 − 10 or $\bar{2}.2227$
	.000003	4.4771 − 10 or $\bar{6}.4771$
	.764	9.8831 − 10 or $\bar{1}.8831$

(b) Divide 6309 by .0009

Logarithm 6300 =	$\bar{3}.7993$	or	$13.7993 - 10$
Logarithm .0009 =	$\bar{4}.9542$	or	$6.9542 - 10$
Log of answer	6.8451		6.8451

Answer is 7,000,000 or 7.00×10^6.

(c) Multiply .0016 by .0131

Logarithm .0016 =	$\bar{3}.2041$	or	$7.2041 - 10$
Logarithm .0131 =	$\bar{2}.1173$	or	$8.1173 - 10$
Log answer	$= \bar{5}.3214$		$15.3214 - 20$ (or $5.3214 - 10$)

Answer is .00002096 or 2.096×10^{-5}

To convert any number into a exponential number on the base 10, it is necessary to use logarithms. Thus, to convert the number 50 into an exponential number we first find the logarithm of 50, which is 1.6990. The logarithm then becomes the exponent of the number 10,

$$50 = 10^{1.6990}$$

The exponential number corresponding to .000005 or 5×10^{-6} is $10^{-5.3010}$. The logarithm of $(5 \times 10^{-6}) = \log 5 + \log 10^{-6} = 0.6990 - 6$. So $5 \times 10^{-6} = 10.^{6990-6} = 10^{-5.3010}$.

The Evaluation of the Hydrogen Ion Concentration (pH values). For convenience, the concentration of the hydrogen ion is often expressed in terms of *p*H values. The *p*H value for any solution is defined as the logarithm of the reciprocal of the concentration of the hydrogen ion, that is, $p\text{H} = \log \frac{1}{(\text{H}^+)}$. The calculation of the *p*H value of any solution for which the concentration of the H^+ ion is known is a simple operation if the text of the foregoing paragraph is understood. For example, let us find the *p*H of a solution, the hydrogen ion concentration of which is 5.3×10^{-6} mole per liter.

$$p\text{H} = \log \frac{1}{5.3 \times 10^{-6}} = \log 1 - \log (5.3 \times 10^{-6})$$
$$= -\log (5.3 \times 10^{-6}) = -\log 5.3 - \log 10^{-6}$$
$$= -0.72 \text{ (approximately)} - (-6) = -0.72 + 6 = 5.28$$

The *p*H value is 5.28 or approximately 5.3. Without regard for the thought processes or definitions involved, the procedure is to find the logarithm of the concentration; change the sign, and the result is the *p*H value. Example: Find the *p*H value of a solution the hydrogen ion concentration of which is 7×10^{-9}.

$$\log (7 \times 10^{-9}) = \log 7 + \log 10^{-9} = 0.85 - 9 = -8.15$$

The *p*H value is accordingly 8.15.

Conversely, the hydrogen ion concentration may be found by reversing the process. Example: Find the hydrogen ion concentration for a solution the *p*H value of which is 4.3.

$$\log \text{ concentration } H^+ \text{ ion} = -4.3 = 0.7 - 5 = 5.7$$

$$= \log 5 + \log 10^{-5}$$

(log of 5 is approximately 0.7)

So the concentration of the hydrogen ion is 5×10^{-5}.

Significant Figures and Precision Necessary in Solving Equations. If the population of a city were given as 576,334. it is obvious that the last three figures have no meaning, for enough deaths and births took place during the making of the record to change these figures an unpredictable amount. It would, therefore, be quite as accurate — even more accurate — to say that the population of the city was 576,000. At a given time, only the first three figures would have any meaning and possibly the third figure would also be of no significance, depending upon the time and method of taking the census. In giving any information in terms of numerical values only as many significant figures should be used as the accuracy warrants. It would be incorrect to say that one's weight is 126.3 pounds if it is known that the scale used was not accurate to more than a pound. Even though the scale registered 126.3 pounds it could not be relied upon to be accurate enough for this figure, so 126 pounds would give better information. Although the scale might be very accurate, the weight of the human body varies sufficiently during the day to make this accuracy of no significance.

In giving the concentration of a substance in solution, again as many significant figures should be used as the experimental information justifies. Thus, if approximately 200 ml. of 1 molar HCl solution were mixed with approximately 800 ml. of water, the concentration of the HCl in the final solution would be expressed as 0.2 molar and not 0.20 molar. The addition of the zero after 0.2 would indicate that the accuracy with which the concentration of the solution was known was about .01 molar, that the solution was not 0.19 molar nor 0.21 molar, but nearer 0.20 molar. Obviously, the manner in which the solution was prepared does not justify this accuracy. To know what figures are to be regarded as significant is often too much to ask of students in the more elementary courses of chemistry. It involves a complete understanding of the methods employed in obtaining the data from an experiment.

The precision employed in making any calculation should depend upon the expected accuracy of the result. For most problems in this course an accuracy of 10 percent in the answer is quite sufficient. In most cases the experimental conditions are such as to render any greater accuracy unnecessary. With this in mind, calculations and algebraic solutions can be greatly simplified. Example: Find the value of X in the following equation. (Only an accuracy within 10 percent is required.)

$$\frac{X}{(3 - X)} = .003$$

By neglecting the X in the term $(3 - X)$ and letting $3 - X$ be approximately equal to 3, we have

$$\frac{X}{3} = .003$$

$$X = .009$$

We neglected X in the term $(3 - X)$ because it could be seen by inspection that X was small as compared with 3. The X can *only* be neglected in a term in which it is added to or subtracted from some number which is much larger than X itself.

Further consideration of such solutions applied to specific examples is given in the main text of this book.

The Solution of Quadratic Equations. All quadratic equations may be expressed in the following form:

$$aX^2 + bX + c = 0,$$

in which equation the coefficients a, b, and c may have positive or negative values. Such an equation has two roots; sometimes these roots are imaginary. However, equations constructed from physical data always have real roots, and of these real roots only those having positive values are of any significance.

The general solution of the above equation is given as

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

The value of X may be obtained by merely substituting the numerical values of a, b, and c into the above form. Example: Solve the equation

$$X^2 + .01X - 4 \times 10^{-6} = 0$$

$$(a = 1,\ b = .01 \text{ and } c = -4 \times 10^{-6})$$

$$X = \frac{-.01 \pm \sqrt{(.01)^2 + 16 \times 10^{-6}}}{2}$$

$$= \frac{-.01 \pm \sqrt{1.16 \times 10^{-4}}}{2}$$

$$= \frac{-.01 \pm .01077}{2}$$

$$= -.010385 \text{ or } +.000385$$

If X in this problem represents some physical quantity such as the concentration of the hydrogen ion, only the positive value of X has a physical significance, and

$$X = 3.85 \times 10^{-4}$$

The Slide Rule. The slide rule is an instrument consisting of two fitted pieces each of which is ruled with lines

which are numbered; the divisions between the different numbers and zero are proportional to the logarithms of the numbers. By sliding one piece along the other, the sum of the logarithms of two numbers can be obtained. Since the process of adding the logarithms of two numbers is the same as multiplying the numbers by each other, the slide rule can be used for multiplication. It follows that the reverse operation of division can also be performed on the slide rule.

Students are strongly urged to obtain a slide rule and use it in making the computations necessary in the course. The solutions of problems are enormously expedited by its use. The ordinary 10-inch slide rule has an accuracy of about one part in 500 which is sufficiently accurate for most work in chemistry. Complete directions for its operation accompany every slide rule.

Proportion. The three statements,

(1) A is proportional to B

(2) $A \propto B$

(3) A = constant $\times B$, or $A = KB$, or $\frac{A}{B} = K$,

are identical in meaning. The statements (2) and (3) are abbreviations of statement (1). In statement (3), K is known as the proportionality constant. If we write

$$d = Ks$$

where d is the distance covered in a given time and s is speed, we are saying that the distance covered in a given time is proportional to the speed.

The rate of formation of hydrogen iodide from its elements, hydrogen and iodine, is expressed by the following equation:

$$\text{rate} = k \times (\textit{concentration of } H_2) \times (\textit{concentration of } I_2)$$

This means that the rate of formation of hydrogen iodide is proportional to the product of the concentrations of the hydrogen and iodine.

Dimensional Formulae. Most physical quantities with which we deal in this text have associated with them dimensional formulae expressed in the fundamental quantities or units of length (l), time (t), mass (m), and temperature (T). Thus, velocity may be expressed in miles per hour, or in centimeters per second, to mention only two of many expressions for velocity. In any event, the dimensional formula for velocity is l/t or lt^{-1}. Acceleration is defined as the change in velocity (v) per unit of time. The dimensional formula for acceleration is lt^{-2} (i.e., $v/t = lt^{-2}$).

The sciences of chemistry and physics use the gram, centimeter, second, degree centigrade system of units. When we adhere to one system we can use more specific fundamental quantities to express dimensional formulae. Thus, instead of time, t, we use the second (sec.); instead of mass (m), the gram (g.); for length we use centimeter (cm.); and for temperature, the degree (deg.).

The following dimensional formulae are those for the centimeter, gram, second (the cgs) system: length (cm.), area (cm.^{2}), volume (cm.^{3}), velocity (cm. sec.$^{-1}$), and acceleration (cm. sec.$^{-2}$). Force is defined as mass $\times$ acceleration; so the dimensions of force are g. cm. sec.$^{-2}$. Work is defined as force $\times$ distance; therefore, the dimensions of work are g. cm.^{2} sec.$^{-2}$. Energy and work have the same dimensions. We know that kinetic energy is equal to $1/2\ mv^2$. The dimensions of this quantity are g. cm.^{2}/sec.^{2}, or g. cm.^{2} sec.$^{-2}$, the same as those for work. Potential energy is equal to mgh, where h is the height above the earth's surface expressed in centimeters and g is the acceleration due to gravity. Potential energy, therefore, has the dimensions g. cm.^{2} sec.$^{-2}$. Concentration may be expressed in grams per milliliter. The dimensions of concentration are g. cm.$^{-3}$.

Very often it is convenient to use derived dimensions instead of the more fundamental ones. For example, we often use gram per liter instead of gram per milliliter for concentration. In this case the dimensions may be written g. liter^{-1} where liter^{-1} is equal to (1000 cm.^{3})$^{-1}$. Also, we often use the term

mole instead of gram. Thus, the concentration can be expressed in terms of mole per liter or mole liter^{-1}.

Pressure is defined as the force per unit area. The dimensions of pressure are, therefore, g. cm. sec.$^{-2}$ cm.$^{-2}$ or g. cm.$^{-1}$ sec.$^{-2}$. If a gas expands under constant pressure and constant temperature, the work done is equal to $p(v_2 - v_1)$ or $p\Delta v$. The dimensions of $p\Delta v$ should be those of work. Multiplying the dimensions of pressure and volume we get g. cm.$^{-1}$ sec.$^{-2}$ $\times$ cm.^{3}, or g. cm.^{2} sec.$^{-2}$, the dimensions of energy or work.

The gas law states that $PV = nRT$, where n is the number of moles of gas and R is a constant. What are the dimensions of R?

$$R = \frac{PV}{nT}$$

The dimensions of both sides of an equation must always be the same. The dimensions of R are therefore,

$$\frac{\text{g. cm.}^{-1}\ \text{sec.}^{-2} \times \text{cm.}^3}{\text{mole} \times \text{degree}} = \text{g. cm.}^2\ \text{sec.}^{-1}\ \text{mole}^{-1}\ \text{degree}^{-1}$$

The fundamental unit of work is the erg. So instead of g. cm.^{2} sec.$^{-2}$ we may write (erg). The dimensions of R are sometimes given as erg mole^{-1} degree^{-1}. In this case the erg is used as a derived unit.

Problems. Mathematical Operations

1. Express the following numbers in the exponential form:

(a)	1,000,000	(m)	.01
(b)	400,000	(n)	.0032
(c)	50,000	(o)	.000007
(d)	9,000	(p)	.00107
(e)	600	(q)	.0000000009
(f)	70	(r)	.00000678
(g)	1,450,000	(s)	0.103
(h)	946,000	(t)	1.0
(i)	59,000	(u)	0.1
(j)	9,627	(v)	.00045
(k)	450	(w)	.000006
(l)	563,200		

2. Express the answers of the following in the exponential form:

(a) Multiply 4.2×10^4 by 3.0×10^4
(b) Multiply 2.5×10^{-2} by 2.0×10^5
(c) Multiply 6.06×10^{23} by 1×10^{-6}
(d) Multiply 4.0×10^{-4} by 7.0×10^{-3}
(e) Multiply .00005 by 10
(f) Multiply .00025 by 400
(g) Multiply .000007 by 1×10^{10}
(h) Multiply 60 by 5,000,000
(i) Multiply 2500 by .0025
(j) Multiply .00003 by .006
(k) Multiply 1×10^6 by .0005

3. Express the answers of the following in the exponential form:

(a) Divide 1×10^6 by 2×10^4
(b) Divide 3×10^4 by 3×10^{-3}
(c) Divide 4.2×10^{-3} by 1.3×10^{-4}
(d) Divide 4.5×10^{-6} by 1.5×10^{-5}
(e) Divide 9×10^{-20} by 2×10^{-15}
(f) Divide 4.2×10^6 by 210,000
(g) Divide 2.5×10^5 by .00005
(h) Divide 6.6×10^{-7} by 1.1×10^5
(i) Divide 5.0×10^{-6} by 2,500,000
(j) Divide 4×10^{-4} by .0008
(k) Divide 64,000 by 2×10^5
(l) Divide 2,500,000 by 5×10^{-8}
(m) Divide .000034 by 1.7×10^3
(n) Divide .00065 by 1.3×10^{-2}

4. Express the answers of the following operations in terms of the significant figures only: (The quantities represent experimental values.)

(a) Add the quantities 1834.56, 50 and 0.765
(b) Subtract 6.0 from 22.45
(c) Subtract 6.00 from 22.45
(d) Multiply 0.675 by $(.02)^2$
(e) Solve for X in the following: $X(6 - X) = .0006$

5. Find the logarithm of the following:

(a) 2156.3
(b) 340
(c) 1.035
(d) .0000067
(e) 67.25
(f) 0.387
(g) .004
(h) 400

6. Give the number (antilogarithm) corresponding to the following logarithms:

(a) 3.6745
(b) 2.4362
(c) .2875
(d) $9.3476 - 10$
(e) $6.4632 - 10$
(f) $\bar{4}.2697$
(g) -2.3628
(h) -0.2756

7. Solve the following expressions with the use of logarithms:

(a) $V = 350 \times \frac{273}{302} \times \frac{745}{760}$ Find V

(b) $N = \frac{6.06 \times 10^{23}}{1000 \times 22.4 \times 760 \times 10^{-6}}$ Find N

(c) $M = \frac{22.4 \times 10^3 \times 2.456}{150}$ Find M

(d) $X = \frac{(3.65)^2 \times 24.5 \times 10^{-4} \times 376.2}{3.0 \times 26.5 \times 500}$ Find X

8. Solve the following expressions; use logarithms where desirable:

(a) $(2.54 \times 10^5)^2$
(b) $(3.6 \times 10^{-4})^2$
(c) $(1.2 \times 10^{-3})^3$
(d) $(6.56 \times 10^2)^2(3.5 \times 10^4)^2$
(e) $(9.2 \times 10^{-2})^2(2.6 \times 10^8)^2$

9. Extract the square root of the following; use logarithms where desirable:

(a) 4×10^{-6}
(b) $(4 \times 10^{-6})^2$
(c) 3.6×10^9
(d) 0.25×10^{-4}
(e) 25×10^{-5}
(f) 6.942×10^3
(g) 24.53×10^{-7}
(h) 1.44×10^{-14}

10. Solve the following equations for X:

(a) $X^2 + 4X + 7 = 0$
(b) $X^2 + 0.15X = 2.53$

(c) $X^2 + (1 \times 10^{-4})X - 3.6 \times 10^{-6} = 0$
(d) $X^2 + (1.8 \times 10^{-5})X - 1.8 \times 10^{-6} = 0$

11. Calculate the *p*H of solutions which contain the following concentration of the hydrogen ion respectively:

(a) 1×10^{-4}
(b) 2×10^{-12}
(c) 3.5×10^{-6}
(d) 1×10^{-7}
(e) 2.56×10^{-5}
(f) 0.1345

12. From the following *p*H values calculate the concentration of the hydrogen ion:

(a) 7.0
(b) 8.4
(c) 5.3
(d) 6.87
(e) 9.25
(f) 2.46

13. Express the following statements in the form of an equation:

(a) At constant temperature, the pressure of a gas varies inversely with the volume.
(b) At constant pressure, the volume of a gas varies directly with the absolute temperature.
(c) At constant volume, the pressure of a gas varies directly with the absolute temperature.
(d) The speed of diffusion of a molecule in the gaseous condition is inversely proportional to the square root of its mass.
(e) The force of attraction between two bodies is directly proportional to the product of their masses and inversely proportional to the square of the distance between them.

14. What is the dimensional formula for (a) density, (b) frequency, and (c) power (energy per second)?

15. Show by dimensional formulae that the following statement is incorrect: "the work done per second is equal to the potential energy of the body."

TABLE 29

IONIZATION CONSTANTS OF WEAK ACIDS

The equilibrium constants given in this and the following tables appear in two forms. In the column to the right, the value of the constant is given in exponential form for convenience when used in calculations involving the half reactions of Table 27. Some of the data have been taken from the International Critical Tables, but most of the data have been obtained from "Oxidation Potentials" by Wendell M. Latimer, published by Prentice-Hall, Inc., 1952. Other data have been selected after a careful evaluation of the literature references.

Acid	Equilibrium	Ionization Constant (at Room Temperature)	
Acetic	$CH_3COOH = H^+ + CH_3COO^-$	1.85×10^{-5}	$10^{-4.7}$
Arsenic	$H_3AsO_4 = H^+ + H_2AsO_4^-$	2.5×10^{-4}	$10^{-3.6}$
Dihydrogen Arsenate ion	$H_2AsO_4^- = H^+ + HAsO_4^{--}$	5.6×10^{-8}	$10^{-7.3}$
Monohydrogen Arsenate ion	$HAsO_4^{--} = H^+ + AsO_4^{---}$	3.0×10^{-13}	$10^{-12.5}$
Arsenous	$H_3AsO_3 = H^+ + H_2AsO_3^-$	6.0×10^{-10}	$10^{-9.3}$
Benzoic	$C_6H_5COOH = H^+ + C_6H_5COO^-$	6.6×10^{-5}	$10^{-4.2}$
Boric	$H_3BO_3 = H^+ + H_2BO_3^-$	6.0×10^{-10}	$10^{-9.3}$
Carbonic	$H_2CO_3 = H^+ + HCO_3^-$	4.2×10^{-7}	$10^{-6.4}$
Bicarbonate ion	$HCO_3^- = H^+ + CO_3^{--}$	4.8×10^{-11}	$10^{-10.3}$
Bisulfate ion	$HSO_4^- = H^+ + SO_4^{--}$	1.26×10^{-2}	$10^{-1.9}$
Chloracetic	$ClCH_2COOH = H^+ + ClCH_2COO^-$	1.4×10^{-3}	$10^{-2.9}$
Chlorous	$HClO_2 = H^+ + ClO_2^-$	1.1×10^{-2}	$10^{-1.0}$
Bicuprate ion	$HCuO_2^- = H^+ + CuO_2^{--}$	8×10^{-14}	$10^{-13.1}$
Cyanic	$HCNO = H^+ + CNO^-$	2.0×10^{-4}	$10^{-3.7}$
Dichloracetic	$Cl_2CHCOOH = H^+ + Cl_2CHCOO^-$	5.5×10^{-2}	$10^{-1.3}$
Formic	$HCOOH = H^+ + HCOO^-$	2.1×10^{-4}	$10^{-3.7}$
Hydrazoic	$HN_3 = H^+ + N_3^-$	1.9×10^{-5}	$10^{-4.7}$
Hydrocyanic	$HCN = H^+ + CN^-$	4.0×10^{-10}	$10^{-9.4}$
Hydrofluoric	$HF = H^+ + F^-$	6.9×10^{-4}	$10^{-3.2}$
Hydrogen peroxide	$H_2O_2 = H^+ + HO_2^-$	2.4×10^{-12}	$10^{-11.6}$
Hydrogen selenide	$H_2Se = H^+ + HSe^-$	1.9×10^{-4}	$10^{-3.7}$
Hydrogen sulfide	$H_2S = H^+ + HS^-$	1.0×10^{-7}	10^{-7}
Bisulfide ion	$HS^- = H^+ + S^{--}$	1.3×10^{-13}	$10^{-12.9}$

Acid	Equilibrium	Ionization Constant (at Room Temperature)	
Hydrogen telluride	$H_2Te = H^+ + HTe^-$	2.5×10^{-3}	$10^{-2.6}$
Bitelluride ion	$HTe^- = H^+ + Te^{--}$	1.0×10^{-11}	10^{-11}
Hypobromous	$HBrO = H^+ + BrO^-$	2×10^{-9}	$10^{-8.7}$
Hypochlorous	$HClO = H^+ + ClO^-$	3.2×10^{-8}	$10^{-7.5}$
Nitrous	$HNO_2 = H^+ + NO_2^-$	4.5×10^{-4}	$10^{-3.3}$
O-Nitrobenzoic	$C_7H_5NO_4 = H^+ + C_7H_4NO_4^-$	6.1×10^{-3}	$10^{-2.2}$
Oxalic	$H_2C_2O_4 = H^+ + HC_2O_4^-$	3.8×10^{-2}	$10^{-1.4}$
Monohydrogen oxalate ion	$HC_2O_4^- = H^+ + C_2O_4^{--}$	5.0×10^{-5}	$10^{-4.3}$
Phenol	$C_6H_5OH = H^+ + C_6H_5O^-$	1.0×10^{-10}	10^{-10}
Phosphoric	$H_3PO_4 = H^+ + H_2PO_4^-$	7.5×10^{-3}	$10^{-2.1}$
Dihydrogen phosphate ion	$H_2PO_4^- = H^+ + HPO_4^{--}$	6.2×10^{-8}	$10^{-7.2}$
Monohydrogen phosphate ion	$HPO_4^{--} = H^+ + PO_4^{---}$	1×10^{-12}	10^{-12}
Phosphorous	$H_3PO_3 = H^+ + H_2PO_3^-$	1.6×10^{-2}	$10^{-1.8}$
Dihydrogen phosphite ion	$H_2PO_3^- = H^+ + HPO_3^{--}$	7.0×10^{-7}	$10^{-6.2}$
Propionic	$C_2H_5COOH = H^+ + C_2H_5COO^-$	1.4×10^{-5}	$10^{-4.9}$
Salicylic	$C_7H_6O_3 = H^+ + C_7H_5O_3^-$	1.1×10^{-3}	10^{-3}
Selenious	$H_2SeO_3 = H^+ + HSeO_3^-$	2.7×10^{-3}	$10^{-2.6}$
Biselenate ion	$HSeO_3^- = H^+ + SeO_3^{--}$	2.5×10^{-7}	$10^{-6.6}$
Sulfurous	$H_2SO_3 = H^+ + HSO_3^-$	1.25×10^{-2}	$10^{-1.9}$
Bisulfite ion	$HSO_3^- = H^+ + SO_3^{--}$	5.6×10^{-8}	$10^{-7.3}$
Tartaric	$C_4H_4O_6H_2 = H^+ + C_4H_4O_6H^-$	1.1×10^{-3}	10^{-3}
Bitartrate ion	$C_4H_4O_6H^- = H^+ + C_4H_4O_6^{--}$	6.9×10^{-5}	$10^{-4.2}$
Telluric	$H_2TeO_4 = H^+ + HTeO_4^-$	6×10^{-7}	$10^{-6.2}$
Bitellurate ion	$HTeO_4^- = H^+ + TeO_4^{--}$	4×10^{-11}	$10^{-10.4}$
Tellurous	$H_2TeO_3 = H^+ + HTeO_3^-$	2×10^{-3}	$10^{-2.7}$
Bitellurite ion	$HTeO_3^- = H^+ + TeO_3^{--}$	1×10^{-8}	10^{-8}
Aluminum hydroxide	$Al(OH)_3 = H^+ + AlO_2^- + H_2O$	4×10^{-13}	$10^{-12.4}$
Antimony hydroxide	$Sb(OH)_3 = H^+ + SbO_2^- + H_2O$	1×10^{-11}	10^{-11}
Chromium hydroxide	$Cr(OH)_3 = H^+ + CrO_2^- + H_2O$	1×10^{-16}	10^{-16}
Cobaltous hydroxide	$Co(OH)_2 = H^+ + HCoO_2^-$	8×10^{-20}	$10^{-19.1}$
Bicuprate ion	$HCuO_2^- = H^+ + CuO_2^{--}$	8×10^{-14}	$10^{-13.1}$
Cupric hydroxide	$H_2CuO_2 = H^+ + HCuO_2^-$	1.5×10^{-16}	$10^{-15.8}$
Lead hydroxide	$Pb(OH)_2 = H^+ + HPbO_2^-$	2×10^{-16}	$10^{-15.7}$
Manganous hydroxide	$Mn(OH)_2 = H^+ + HMnO_2^-$	1×10^{-19}	10^{-19}
Mercuric hydroxide	$Hg(OH)_2 = H^+ + HHgO_2^-$	1×10^{-15}	10^{-15}
Nickelous hydroxide	$Ni(OH)_2 = H^+ + HNiO_2^-$	6×10^{-19}	$10^{-18.2}$
Silver hydroxide	$AgOH = H^+ + AgO^-$	2×10^{-18}	$10^{-17.7}$
Stannous hydroxide	$Sn(OH)_2 = H^+ + HSnO_2^-$	4×10^{-15}	$10^{-14.4}$
Zinc hydroxide	$Zn(OH)_2 = 2H^+ + ZnO_2^{--}$	1×10^{-29}	10^{-29}
	$Zn(OH)_{2(s)} = Zn(OH)^+ + OH^-$	1.2×10^{-12}	$10^{-11.9}$
	$Zn(OH)^+ = Zn^{++} + OH^-$	4×10^{-5}	$10^{-4.4}$

Table 30

Ionization Constants of Weak Bases

Base	Equilibrium	Ionization Constant (at Room Temperature)	
Ammonium hydroxide	$NH_4OH = NH_4^+ + OH^-$	1.8×10^{-5}	$10^{-4.7}$
Methyl ammonium hydroxide	$CH_3NH_3OH = CH_3NH_3^+ + OH^-$	5×10^{-4}	$10^{-3.3}$
Dimethyl ammonium hydroxide	$(CH_3)_2NH_2OH = (CH_3)_2NH_2^+ + OH^-$	7.4×10^{-4}	$10^{-3.1}$
Trimethyl ammonium hydroxide	$(CH_3)_3NHOH = (CH_3)_3NH^+ + OH^-$	7.4×10^{-5}	$10^{-4.1}$
Ethyl ammonium hydroxide	$C_2H_5NH_3OH = C_2H_5NH_3^+ + OH^-$	5.6×10^{-4}	$10^{-3.3}$
Phenyl ammonium hydroxide	$C_6H_5NH_3OH = C_6H_5NH_3^+ + OH^-$	4.6×10^{-10}	$10^{-9.3}$
Hydrazine hydroxide	$H_2N \cdot NH_3OH = H_2N \cdot NH_3^+ + OH^-$	9.8×10^{-7}	10^{-6}
Zinc hydroxide	(1) $Zn(OH)_{2(s)} = Zn(OH)^+ + OH^-$ K = $1,2 \times 10^{-12}$ and $10^{-11.9}$ (2) $Zn(OH)^+ = Zn^{++} + OH^-$ K = 4×10^{-5} and $4 \times 10^{-4.4}$		

Table 31

Solubility Product Constants at Room Temperature

Substance	Equilibrium	Solubility Product Constant	
Acetates			
Silver acetate	$CH_3COOAg_{(s)} = Ag^+ + CH_3COO^-$	4×10^{-3}	$10^{-2.4}$
Bromates			
Silver bromate	$AgBrO_{3(s)} = Ag^+ + BrO_3^-$	6×10^{-5}	$10^{-4.2}$
Bromides			
Cuprous bromide	$CuBr_{(s)} = Cu^+ + Br^-$	6×10^{-9}	$10^{-8.2}$
Lead bromide	$PbBr_{2(s)} = Pb^{++} + 2\,Br^-$	4.6×10^{-6}	$10^{-5.3}$
Mercurous bromide	$Hg_2Br_{2(s)} = Hg_2^{++} + 2Br^-$	1.3×10^{-22}	$10^{-21.9}$
Silver bromide	$AgBr_{(s)} = Ag^+ + Br^-$	5×10^{-13}	$10^{-12.3}$
Carbonates			
Barium carbonate	$BaCO_{3(s)} = Ba^{++} + CO_3^{--}$	1.6×10^{-9}	$10^{-8.8}$
Cadmium carbonate	$CdCO_{3(s)} = Cd^{++} + CO_3^{--}$	5.2×10^{-12}	$10^{-11.3}$
Calcium carbonate	$CaCO_{3(s)} = Ca^{++} + CO_3^{--}$	6.9×10^{-9}	$10^{-8.2}$
Cobalt carbonate	$CoCO_{3(s)} = Co^{++} + CO_3^{--}$	8×10^{-13}	$10^{-12.1}$

Substance	Equilibrium	Solubility Product Constant	
Cupric carbonate	$CuCO_{3(s)} = Cu^{++} + CO_3^{--}$	2.5×10^{-10}	$10^{-9.6}$
Lead carbonate	$PbCO_{3(s)} = Pb^{++} + CO_3^{--}$	1.5×10^{-13}	$10^{-12.8}$
Magnesium carbonate	$MgCO_{3(s)} = Mg^{++} + CO_3^{--}$	4×10^{-5}	$10^{-4.4}$
Manganous carbonate	$MnCO_{3(s)} = Mn^{++} + CO_3^{--}$	9×10^{-11}	$10^{-10.1}$
Mercurous carbonate	$Hg_2CO_{3(s)} = Hg_2^{++} + CO_3^{--}$	9×10^{-17}	$10^{-16.1}$
Nickelous carbonate	$NiCO_{3(s)} = Ni^{++} + CO_3^{--}$	1.4×10^{-7}	$10^{-6.8}$
Silver carbonate	$Ag_2CO_{3(s)} = 2Ag^{+} + CO_3^{--}$	8.2×10^{-12}	$10^{-11.1}$
Strontium carbonate	$SrCO_{3(s)} = Sr^{++} + CO_3^{--}$	7×10^{-10}	$10^{-9.2}$
Zinc carbonate	$ZnCO_{3(s)} = Zn^{++} + CO_3^{--}$	2×10^{-10}	$10^{-9.7}$
Chlorides			
Cuprous chloride	$CuCl_{(s)} = Cu^{+} + Cl^{-}$	3.2×10^{-7}	$10^{-6.5}$
Lead chloride	$PbCl_{2(s)} = Pb^{++} + 2Cl^{-}$	1.6×10^{-5}	$10^{-4.8}$
Mercurous chloride	$Hg_2Cl_{2(s)} = Hg_2^{++} + 2Cl^{-}$	1.1×10^{-18}	$10^{-17.9}$
Silver chloride	$AgCl_{(s)} = Ag^{+} + Cl^{-}$	2.8×10^{-10}	$10^{-9.6}$
Chromates			
Barium chromate	$BaCrO_{4(s)} = Ba^{++} + CrO_4^{--}$	8.5×10^{-11}	$10^{-10.}$
Calcium chromate	$CaCrO_{4(s)} = Ca^{++} + CrO_4^{--}$	7.1×10^{-4}	$10^{-3.2}$
Lead chromate	$PbCrO_{4(s)} = Pb^{++} + CrO_4^{--}$	2.0×10^{-16}	$10^{-15.}$
Mercurous chromate	$Hg_2CrO_{4(s)} = Hg_2^{++} + CrO_4^{--}$	2×10^{-9}	$10^{-8.71}$
Silver chromate	$Ag_2CrO_{4(s)} = 2Ag^{+} + CrO_4^{--}$	1.9×10^{-12}	$10^{-11.7}$
Strontium chromate	$SrCrO_{4(s)} = Sr^{++} + CrO_4^{--}$	3.6×10^{-5}	$10^{-4.4}$
Cyanides			
Mercurous cyanide	$Hg_2(CN)_{2(s)} = Hg_2^{++} + 2CN^{-}$	5×10^{-40}	$10^{-39.3}$
Silver cyanide	$AgCN_{(s)} = Ag^{+} + CN^{-}$	1.6×10^{-14}	$10^{-13.8}$
Fluorides			
Barium fluoride	$BaF_{2(s)} = Ba^{++} + 2F^{-}$	2.4×10^{-5}	$10^{-4.6}$
Calcium fluoride	$CaF_{2(s)} = Ca^{++} + 2F^{-}$	1.7×10^{-10}	$10^{-9.8}$
Lead fluoride	$PbF_{2(s)} = Pb^{++} + 2F^{-}$	4×10^{-8}	$10^{-7.4}$
Magnesium fluoride	$MgF_{2(s)} = Mg^{++} + 2F^{-}$	8×10^{-8}	$10^{-7.1}$
Strontium fluoride	$SrF_{2(s)} = Sr^{++} + 2F^{-}$	7.9×10^{-10}	$10^{-9.1}$
Hydroxides			
Aluminum hydroxide	$Al(OH)_{3(s)} = Al^{+++} + 3OH^{-}$	5×10^{-33}	$10^{-32.3}$
Cadmium hydroxide	$Cd(OH)_{2(s)} = Cd^{++} + 2OH^{-}$	2.0×10^{-14}	$10^{-13.7}$
Chromic hydroxide	$Cr(OH)_{3(s)} = Cr^{+++} + 3OH^{-}$	7×10^{-31}	$10^{-30.2}$
Chromous hydroxide	$Cr(OH)_{2(s)} = Cr^{++} + 2OH^{-}$	1×10^{-17}	10^{-17}
Cobaltic hydroxide	$Co(OH)_{3(s)} = Co^{+++} + 3OH^{-}$	1×10^{-43}	10^{-43}
Cobaltous hydroxide	$Co(OH)_{2(s)} = Co^{++} + 2OH^{-}$	2.5×10^{-16}	$10^{-15.6}$
Cupric hydroxide	$Cu(OH)_{2(s)} = Cu^{++} + 2OH^{-}$	1.6×10^{-19}	$10^{-18.8}$
Ferric hydroxide	$Fe(OH)_{3(s)} = Fe^{+++} + 3OH^{-}$	6×10^{-38}	$10^{-37.2}$
Ferrous hydroxide	$Fe(OH)_{2(s)} = Fe^{++} + 2OH^{-}$	2×10^{-15}	$10^{-14.7}$
Lead hydroxide	$Pb(OH)_{2(s)} = Pb^{++} + 2OH^{-}$	4×10^{-15}	$10^{-14.4}$
Magnesium hydroxide	$Mg(OH)_{2(s)} = Mg^{++} + 2OH^{-}$	8.9×10^{-12}	10^{-11}

Substance	Equilibrium	Solubility Product Constant	
Manganese hydroxide	$Mn(OH)_{2(s)} = Mn^{++} + 2OH^-$	2×10^{-13}	$10^{-12.7}$
Manganic hydroxide	$Mn(OH)_{3(s)} = Mn^{+++} + 3OH^-$	1×10^{-36}	10^{-36}
Mercuric hydroxide	$HgO_{(s)} + H_2O = Hg^{++} + 2OH^-$	3×10^{-26}	$10^{-25.5}$
Nickel hydroxide	$Ni(OH)_{2(s)} = Ni^{++} + 2OH^-$	1.6×10^{-16}	$10^{-15.8}$
Silver hydroxide	$\frac{1}{2}Ag_2O_{(s)} + \frac{1}{2}H_2O = Ag^+ + OH^-$	1×10^{-8}	$10^{-7.7}$
Stannous hydroxide	$Sn(OH)_{2(s)} = Sn^{++} + 2OH^-$	3×10^{-27}	$10^{-26.5}$
Zinc hydroxide	$Zn(OH)_{2(s)} = Zn^{++} + 2OH^-$	5×10^{-17}	$10^{-16.3}$
Iodates			
Barium iodate	$Ba(IO_3)_{2(s)} = Ba^{++} + 2IO_3^-$	1.3×10^{-9}	$10^{-8.9}$
Calcium iodate	$Ca(IO_3)_{2(s)} = Ca^{++} + 2IO_3^-$	1.7×10^{-6}	$10^{-5.8}$
Cupric iodate	$Cu(IO_3)_{2(s)} = Cu^{++} + 2IO_3^-$	1.4×10^{-7}	$10^{-6.9}$
Lead iodate	$Pb(IO_3)_{2(s)} = Pb^{++} + 2IO_3^-$	2.6×10^{-13}	$10^{-12.6}$
Mercuric iodate	$Hg(IO_3)_{2(s)} = Hg^{++} + 2IO_3^-$	3×10^{-13}	$10^{-12.5}$
Mercurous iodate	$Hg_2(IO_3)_{2(s)} = Hg_2^{++} + 2IO_3^-$	1.9×10^{-14}	$10^{-13.7}$
Silver iodate	$AgIO_{3(s)} = Ag^+ + IO_3^-$	3×10^{-8}	$10^{-7.5}$
Iodides			
Cuprous iodide	$CuI_{(s)} = Cu^+ + I^-$	1×10^{-12}	10^{-12}
Lead iodide	$PbI_{2(s)} = Pb^{++} + 2I^-$	8.3×10^{-9}	$10^{-8.1}$
Mercurous iodide	$Hg_2I_{2(s)} = Hg_2^{++} + 2I^-$	4×10^{-29}	$10^{-28.4}$
Silver iodide	$AgI_{(s)} = Ag^+ + I^-$	8.5×10^{-17}	$10^{-16.1}$
Thallous iodide	$TlI_{(s)} = Tl^+ + I^-$	2.5×10^{-8}	$10^{-7.6}$
Oxalates			
Barium oxalate	$BaC_2O_{4(s)} = Ba^{++} + C_2O_4^{--}$	1.5×10^{-8}	$10^{-7.8}$
Cadmium oxalate	$CdC_2O_{4(s)} = Cd^{++} + C_2O_4^{--}$	1.5×10^{-8}	$10^{-7.8}$
Calcium oxalate	$CaC_2O_{4(s)} = Ca^{++} + C_2O_4^{--}$	1.3×10^{-9}	$10^{-8.8}$
Cupric oxalate	$CuC_2O_{4(s)} = Cu^{++} + C_2O_4^{--}$	3×10^{-8}	$10^{-7.5}$
Ferrous oxalate	$FeC_2O_{4(s)} = Fe^{++} + C_2O_4^{--}$	2×10^{-7}	$10^{-6.7}$
Lead oxalate	$PbC_2O_{4(s)} = Pb^{++} + C_2O_4^{--}$	8.3×10^{-12}	$10^{-11.1}$
Magnesium oxalate	$MgC_2O_{4(s)} = Mg^{++} + C_2O_4^{--}$	8.6×10^{-5}	$10^{-4.1}$
Manganic oxalate	$Mn_2(C_2O_4)_{3(s)} = 2Mn^{+++} + 3C_2O_4^{--}$	7×10^{-20}	$10^{-19.2}$
Manganous oxalate	$MnC_2O_{4(s)} = Mn^{++} + C_2O_4^{--}$	1×10^{-15}	10^{-15}
Mercurous oxalate	$Hg_2C_2O_{4(s)} = Hg_2^{++} + C_2O_4^{--}$	1×10^{-13}	10^{-13}
Silver oxalate	$Ag_2C_2O_{4(s)} = 2Ag^+ + C_2O_4^{--}$	1×10^{-11}	10^{-11}
Strontium oxalate	$SrC_2O_{4(s)} = Sr^{++} + C_2O_4^{--}$	5.6×10^{-8}	$10^{-7.2}$
Zinc oxalate	$ZnC_2O_{4(s)} = Zn^{++} + C_2O_4^{--}$	1.5×10^{-9}	$10^{-8.8}$
Sulfates			
Barium sulfate	$BaSO_{4(s)} = Ba^{++} + SO_4^{--}$	1.5×10^{-9}	$10^{-8.8}$
Calcium sulfate	$CaSO_{4(s)} = Ca^{++} + SO_4^{--}$	2.4×10^{-5}	$10^{-4.7}$
Lead sulfate	$PbSO_{4(s)} = Pb^{++} + SO_4^{--}$	1.3×10^{-8}	$10^{-7.8}$
Strontium sulfate	$SrSO_{4(s)} = Sr^{++} + SO_4^{--}$	7.6×10^{-7}	$10^{-6.1}$

Substance	Equilibrium	Solubility Product Constant	
Sulfides			
Bismuth sulfide	$Bi_2S_{3(s)} = 2Bi^{+++} + 3S^{--}$	1×10^{-70}	10^{-70}
Cadmium sulfide	$CdS_{(s)} = Cd^{++} + S^{--}$	6×10^{-27}	$10^{-26.2}$
Cobalt sulfide	$CoS_{(s)} = Co^{++} + S^{--}$	5×10^{-22}	$10^{-21.3}$
Cupric sulfide	$CuS_{(s)} = Cu^{++} + S^{--}$	4×10^{-36}	$10^{-35.4}$
Ferrous sulfide	$FeS_{(s)} = Fe^{++} + S^{--}$	4×10^{-17}	$10^{-16.4}$
Lead sulfide	$PbS_{(s)} = Pb^{++} + S^{--}$	4×10^{-26}	$10^{-25.4}$
Manganous sulfide	$MnS_{(s)} = Mn^{++} + S^{--}$	8×10^{-14}	$10^{-13.1}$
Mercuric sulfide	$HgS_{(s)} = Hg^{++} + S^{--}$	1×10^{-50}	10^{-50}
Mercurous sulfide	$Hg_2S_{(s)} = Hg_2^{++} + S^{--}$	1×10^{-45}	10^{-45}
Nickelous sulfide	$NiS_{(s)} = Ni^{++} + S^{--}$	1×10^{-22}	10^{-22}
Silver sulfide	$Ag_2S_{(s)} = 2Ag^{+} + S^{--}$	1×10^{-50}	10^{-50}
Thallous sulfide	$Tl_2S_{(s)} = 2Tl^{+} + S^{--}$	1×10^{-22}	10^{-22}
Zinc sulfide	$ZnS_{(s)} = Zn^{++} + S^{--}$	1×10^{-20}	10^{-20}
Thiocyanates			
Cuprous thiocyanate	$CuCNS_{(s)} = Cu^{+} + CNS^{-}$	4×10^{-14}	$10^{-13.4}$
Mercurous thiocyanate	$Hg_2(CNS)_{2(s)} = Hg_2^{++} + 2CNS^{-}$	3×10^{-20}	$10^{-19.5}$
Silver thiocyanate	$AgCNS_{(s)} = Ag^{+} + CNS^{-}$	1×10^{-12}	10^{-12}

TABLE 32

DISSOCIATION CONSTANTS OF COMPLEX IONS

Equilibrium		Dissociation Constant	
AlF_6^{---}	$= Al^{+++} + 6F^-$	1.5×10^{-20}	$10^{-19.8}$
AlF_5^{--}	$= Al^{+++} + 5F^-$	4.3×10^{-20}	$10^{-19.4}$
AlF_4^-	$= Al^{+++} + 4F^-$	2×10^{-18}	$10^{-17.7}$
$Cd(NH_3)_4^{++}$	$= Cd^{++} + 4NH_3$	1×10^{-7}	10^{-7}
$Cd(CN)_4^{--}$	$= Cd^{++} + 4CN^-$	1×10^{-19}	10^{-19}
CdI_4^{--}	$= Cd^{++} + 4I^-$	5×10^{-7}	$10^{-6.3}$
$CdCl_3^-$	$= Cd^{++} + 3Cl^-$	4×10^{-3}	$10^{-2.4}$
$Cr(CNS)_6$	$= Cr^{+++} + 3CNS^-$	1.6×10^{-6}	$10^{-5.7}$
$Co(NH_3)_6^{++}$	$= Co^{++} + 6NH_3$	1.25×10^{-5}	$10^{-4.8}$
$Co(NH_3)_6^{+++}$	$= Co^{+++} + 6NH_3$	2.2×10^{-34}	$10^{-33.7}$
$Co(NH_3)_5H_2O^{+++}$	$= Co^{+++} + 5NH_3 + H_2O$	1.6×10^{-35}	$10^{-34.8}$
$Co(NH_3)_5Cl^{++}$	$= Co^{+++} + 5NH_3 + Cl^-$	1×10^{-38}	10^{-38}
$Cu(CN)_2^-$	$= Cu^+ + 2CN^-$	1×10^{-16}	10^{-16}
$Cu(NH_3)^+$	$= Cu^+ + NH_3$	7×10^{-7}	$10^{-6.2}$
$Cu(NH_3)_2^+$	$= Cu^+ + 2NH_3$	1.4×10^{-11}	$10^{-10.8}$
$Cu(CN)_4^{---}$	$= Cu^+ + 4CN^-$	2×10^{-27}	$10^{-26.7}$
$Cu(NH_3)_4^{++}$	$= Cu^{++} + 4NH_3$	5×10^{-15}	$10^{-14.3}$
$Cu(C_2O_4)_2^{--}$	$= Cu^{++} + 2C_2O_4^{--}$	5×10^{-11}	$10^{-10.3}$
$Fe(CN)_6^{----}$	$= Fe^{++} + 6CN^-$	1×10^{-35}	10^{-35}
$Fe(CN)_6^{---}$	$= Fe^{+++} + 6CN^-$	1×10^{-42}	10^{-42}
FeF_5^{--}	$= Fe^{+++} + 5F^-$	5×10^{-16}	$10^{-15.3}$
$FeCNS^{++}$	$= Fe^{+++} + CNS^-$	1×10^{-3}	10^{-3}
$Fe(CNS)_3$	$= Fe^{+++} + 3CNS^-$	3×10^{-6}	$10^{-5.5}$
$Fe(CNS)_6^{---}$	$= Fe^{+++} + 6CNS^-$	8×10^{-10}	$10^{-9.1}$
$PbCl_3^-$	$= Pb^{++} + 3Cl^-$	4.2×10^{-2}	$10^{-1.4}$
PbI_3^-	$= Pb^{++} + 3I^-$	3.6×10^{-6}	$10^{-5.4}$
$Mn(C_2O_4)^+$	$= Mn^{+++} + C_2O_4^{--}$	1×10^{-10}	10^{-10}
$Mn(C_2O_4)_2^-$	$= Mn^{+++} + 2C_2O_4^{--}$	2.5×10^{-17}	$10^{-16.6}$
$Mn(C_2O_4)_3^{---}$	$= Mn^{+++} + 3C_2O_4^{--}$	7×10^{-20}	$10^{-19.2}$
$Hg(CN)_4^{--}$	$= Hg^{++} + 4CN^-$	4×10^{-42}	$10^{-41.4}$
HgI_4^{--}	$= Hg^{++} + 4I^-$	5×10^{-31}	$10^{-30.3}$
$HgBr_4^{--}$	$= Hg^{++} + 4Br^-$	2.3×10^{-22}	$10^{-21.7}$
$HgCl_4^{--}$	$= Hg^{++} + 4Cl^-$	1×10^{-16}	10^{-16}
$Hg(CNS)_4^{--}$	$= Hg^{++} + 4CNS^-$	5×10^{-20}	$10^{-19.3}$
$Ni(NH_3)_4^{++}$	$= Ni^{++} + 4NH_3$	1×10^{-8}	10^{-8}
$Ni(NH_3)_6^{++}$	$= Ni^{++} + 6NH_3$	1.8×10^{-9}	$10^{-8.7}$
$Ni(CN)_4^{--}$	$= Ni^{++} + 4CN^-$	1×10^{-22}	10^{-22}
$Ag(SO_3)_2^{---}$	$= Ag^+ + 2SO_3^{--}$	2×10^{-9}	$10^{-8.7}$
$Ag(NH_3)_2^+$	$= Ag^+ + 2NH_3$	6×10^{-8}	$10^{-7.2}$
$Ag(S_2O_3)_2^{---}$	$= Ag^+ + 2S_2O_3^{--}$	6×10^{-14}	$10^{-13.2}$
$Ag(CN)_2^-$	$= Ag^+ + 2CN^-$	1.8×10^{-19}	$10^{-18.7}$
SnF_6^{--}	$= Sn^{++++} + 6F^-$	1×10^{-18}	10^{-18}
$Zn(NH_3)_4^{++}$	$= Zn^{++} + 4NH_3$	3.4×10^{-10}	$10^{-9.5}$
$Zn(CN)_4^{--}$	$= Zn^{++} + 4CN^-$	1×10^{-18}	10^{-18}

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ANSWERS TO PROBLEMS

CHAPTER 1. Pages 21–24.

(8) 1.37 M.
(9) 0.1 mole.
(10) 0.392 g.
(11) .0565 M.
(12) (a) 0.1 mole; (b) 0.1 M; (c) 0.2 M.
(13) (a) 3.15 g.; (b) 245.2 g.; (c) 5.30 g.; (d) 0.204 g.; (e) 13.0 g.
(14) (a) 1709 ml.; (b) 1176 ml.; (c) 368 ml.; (d) 310 ml.; (e) 40 ml.
(15) (a) 20 ml.; (b) 475 ml.; (c) 54 ml.; (d) 140 ml.; (e) 0.4 ml.
(16) 75 ml. 0.1 M $AgNO_3$ and 175 ml. water.
(17) 75 ml.
(18) 37.5 ml.
(19) 10 ml.
(20) 7.5 ml.
(21) (a) 17.4 M; (b) 6.15 M; (c) 13.15 M; (d) 4.72 M.
(22) 152 cm.
(23) (a) 92.8%; (b) 86.6%; (c) 89.6%; (d) 90.7%.
(24) 6.4 g.
(25) Fe_2O_3.
(26) 478.4 g.
(27) 6.6 g.
(28) 1398 lbs.
(29) 2 atoms; Cu_2S.
(30) Cr_2O_3.
(31) 19.9.
(32) 11.0 M.
(33) 9.1 ml.
(34) 58.9 ml.
(35) 200 ml. each of $AgNO_3$, $Pb(NO_3)_2$ and $Hg_2(NO_3)_2$ solutions.
(36) (a) $\rho_1 v_1^2/M = \rho_2 v_2^2/M$; $v_1^2/v_2^2 = \rho_2/\rho_1$; or $v_1/v_2 = \sqrt{\rho_2/\rho_1}$
$\rho_2/\rho_1 = 750/760 \times 273/311 = 0.866$
$v_1/v_2 = 0.93$; v_2 equals 215 miles per hour.
(b) $\rho_1 v^2/M_1 = \rho_2 v^2/M_2$ or $M_2/M_1 = \rho_2/\rho_1 = 0.866$
$M_2 = 86{,}600$ pounds.
(37) Smaller load on a humid day. The molecular weight of water

vapor is less than that of either oxygen or nitrogen. ρ is therefore smaller.

CHAPTER 2. Pages 65–66.

(1) (a) Xe; (b) Xe; (c) Kr; (d) n or He; (e) Ne; (f) none; (g) none; (h) Xe; (i) Ne; (j) none.

(4) Na.

CHAPTER 4. Pages 86–87.

(4) $\gamma = \left(\frac{1}{3^2} - \frac{1}{n^2}\right)$, where n is greater than 3.

(6) (a) 2; (b) 3.

CHAPTER 6. Pages 121–123.

(2) 256 times faster.

(4) 16 times faster.

(11) 105.

(12) $K = 0.4$; (1) $d = 3$; (2) $d = 1.5$; (3) $a = 1.5$; (4) $a = 6$; (5) $b = 8$; (6) $b = 16$; (7) $d = 24$; (8) $d = 96$.

(13) (1) $\frac{(H^+)(CN^-)}{(HCN)} = K$; (2) $\frac{(NH_4^+)(OH^-)}{(NH_4OH)} = K$;

(3) $\frac{(H^+)^2(S^{--})}{(H_2S)} = K$; (4) $\frac{(Fe^{++})^2(Hg^{++})^2}{(Hg_2^{++})(Fe^{+++})^2} = K$;

(5) $\frac{(CO)(H_2O)}{(CO_2)(H_2)} = K$; (6) $\frac{(NO)^2(O_2)}{(NO_2)^2} = K$;

(7) $\frac{(NH_3)^2}{(N_2)(H_2)^3} = K$.

(17) Absorbed.

(18) More soluble.

CHAPTER 7. Pages 152–155.

(7) (a) 5; (b) 9; (c) 1; (d) 7.38; (e) 2.1.

(8) (a) $1.36 \times 10^{-3}\ M$; (b) $4.3 \times 10^{-4}\ M$; (c) $4.3 \times 10^{-3}\ M$; (d) $4.5 \times 10^{-6}\ M$; (e) $1.91 \times 10^{-3}\ M$; (f) $2 \times 10^{-3}\ M$; (g) $1.4 \times 10^{-4}\ M$; (h) $1 \times 10^{-2}\ M$; (i) $1.27 \times 10^{-6}\ M$; (j) $5.5 \times 10^{-5}\ M$.

(9) (a) $4.2 \times 10^{-3}\ M$; (b) $1.3 \times 10^{-3}\ M$; (c) $4.2 \times 10^{-4}\ M$;

(d) $1.3 \times 10^{-4}\ M$; (e) $8.5 \times 10^{-4}\ M$; (f) $2.2 \times 10^{-3}\ M$;
(g) $1.2 \times 10^{-2}\ M$; (h) $7.5 \times 10^{-3}\ M$; (i) $9.6 \times 10^{-7}\ M$.

(10) (a) 1.85×10^{-5}; (b) 1.84×10^{-5}; (c) 1.80×10^{-5};
(d) 1.80×10^{-5}; (e) 4.6×10^{-4}; (f) 4.2×10^{-10};
(g) 4.2×10^{-10}

(11) $8 \times 10^{-4}\ M$ each.

(12) $(H^+) = 2.5 \times 10^{-5}\ M$; $(Ac^-) = 2.4 \times 10^{-2}\ M$.

(13) (a) .068; (b) .0002; (c) .019; (d) .03; (e) .08.

(14) .074 M.

(15) $5.7 \times 10^{-4}\ M$.

(16) 0.72 M.

(17) 0.18 mole.

(18) $8.5 \times 10^{-6}\ M$.

(19) $1.2 \times 10^{-5}\ M$.

(20) (a) 1×10^{-5}; (b) $3.2 \times 10^{-4}\ M$; (c) .032; (d) $1 \times 10^{-5}\ M$.

(21) .011 M.

(22) .04 M.

(23) $5.5 \times 10^{-6}\ M$.

(24) $1.9 \times 10^{-6}\ M$.

(25) $9 \times 10^{-6}\ M$.

(26) .02 M.

(27) $2.6 \times 10^{-5}\ M$.

(28) $2.9 \times 10^{-5}\ M$.

(29) (a) 1; (b) 1.56; (c) 2.87; (d) 4.75.

(30) Condition necessary for correct answer is that

$$\frac{(Ac^-)}{(HAc)} = 0.185$$

(31) (a) One-half; (b) .05 M; (c) .05 M; (d) $1.8 \times 10^{-5}\ M$.

(32) First addition of NaOH: (a) one-tenth; (b) .01 M;
(c) .09 M; (d) $1.67 \times 10^{-4}\ M$; (e) 3.78.

(33) (a) 10^{-4}; (b) 10^{-6}; (c) 10^{-7}; (d) 10^{-9}; (e) 10^{-10}.

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(3) $1.67 \times 10^{-7}\ M$.

(14) (a) 2.8×10^{-10}; (b) 5×10^{-13}; (c) 8.5×10^{-17}; (d) 1.5×10^{-9};
(e) 1.83×10^{-12}; (f) 6.9×10^{-9}; (g) 7.9×10^{-10}.

(15) (a) 7.6×10^{-4} g. per 100 ml.; (b) 7.9×10^{-4} g. per 100 ml.;
(c) 2.59×10^{-3} g. per 100 ml.; (d) 2.3×10^{-9} g. per 100 ml.;
(e) 0.104 g. per 100 ml.; (f) 1.6×10^{-2} g. per 100 ml.;

(g) 1.9×10^{-5} g. per 100 ml.;
(h) 1.69×10^{-6} g. per 100 ml.

(16) 2.1×10^{-9} mole per liter. 6.8×10^{-8} g. per 200 ml.
(17) 7.24×10^{-5} g. per 100 ml.
(18) (a) 0.30 g.; (b) 4×10^{-11} mole.
(19) (a) 2.8×10^{-9} mole; (b) 1.4×10^{-9} mole.
(20) (a) 5×10^{-12} M; (b) 4.3×10^{-6} M; (c) 8.5×10^{-14}.
(21) (a) $(Pb^{++}) = 1.25 \times 10^{-3}$ M, $(I^-) = 2.5 \times 10^{-3}$ M;
(c) 8×10^{-9}.
(22) (a) 3.6×10^{-5} M; (b) 4.6×10^{-3} g.
(23) 4.5×10^{-3} g. per 200 ml.
(24) 1×10^{-4} M.
(25) 1.16×10^{-4} g.
(26) 2.8×10^{-5}.
(27) 1×10^{-3} M; 1.8×10^{-6} M.
(28) (a) 3.8×10^{-7} g.; (b) 9.0×10^{-6} g.
(29) (a) 2.8×10^{-9} mole; (b) 1.67×10^{-5} mole;
(c) 1.67×10^{-5} mole; (d) 2.8×10^{-9} mole;
(e) 1.25×10^{-5} mole.
(30) 560.
(31) (a) 8.5×10^{-16} M; (b) 2.8×10^{-9} M; (c) AgI;
(d) 3.0×10^{-8} M; (e) $3 \times 10^{-5}\%$; (f) 3.3×10^{6};
(g) 5.6×10^{-9} M; 1.5×10^{-8} M; (h) 3.3×10^{6}.
(32) (a) 8.5×10^{-15} M; (b) 9.1×10^{-4} M; (c) AgI;
(d) 9.3×10^{-14} M; (e) 1.1×10^{11}; (f) 1.29×10^{-3} M;
(g) 6.6×10^{-14} M; (h) 7.6×10^{10};
(i) $\dfrac{(Pb^{++})^{\frac{1}{2}}}{(Ag^+)} = 1.07 \times 10^{12}$;
(j) Due to the fact that $\dfrac{(Pb^{++})^{\frac{1}{2}}}{(Ag^+)}$ rather than $\dfrac{(Pb^{++})}{(Ag^+)}$ is constant.
(33) 0.13 mole.
(34) .083 mole.
(35) 2.14 g. per 50 ml.
(36) 70.5 g.
(37) 22 moles per liter — impossible.

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(8) 5×10^{-5} M; No.
(9) $(S^{--}) = 1.3 \times 10^{-13}$ M; $(H^+) = 7.1 \times 10^{-5}$ M.

(10) $(H^+) = 6.9 \times 10^{-4}\ M$.
(11) (a) $2.05 \times 10^{-4}\ M$; (b) $6.5 \times 10^{-5}\ M$; (c) $3.2 \times 10^{-5}\ M$; (d) $4.9 \times 10^{-6}\ M$; (e) $.016\ M$; (f) $.024\ M$; (g) $4.6 \times 10^{-2}\ M$.
(12) (a) $1.3 \times 10^{-13}\ M$; (b) $1.3 \times 10^{-15}\ M$; (c) $1.3 \times 10^{-17}\ M$; (d) $1.3 \times 10^{-19}\ M$; (e) $1.3 \times 10^{-21}\ M$.
(14) (a) $0.3\ M$; (b) $1.44 \times 10^{-20}\ M$; (c) Yes; (d) No.
(15) $(Cd^{++}) = 6 \times 10^{-8}\ M$.
(16) 3.6×10^{-7} mole Pb^{++} ion per 100 ml.
(17) (a) $5 \times 10^{-33}\ M$; (b) $1.7 \times 10^{-22}\ M$; (c) $1.3 \times 10^{-17}\ M$; (d) $4 \times 10^{-47}\ M$; (e) $1.3 \times 10^{-23}\ M$.
(18) $(H^+) < 2.4 \times 10^{-3}\ M$.
(19) $(S^{--}) = 7 \times 10^{-16}\ M$.
(20) (a) $1.6 \times 10^{-2}\ M$; (b) $1.6 \times 10^{-2}\ M$; (c) $6.2 \times 10^{-8}\ M$; (d) about $4 \times 10^{-18}\ M$.
(21) 7.2×10^{-16} mole Cu^{++} per 200 ml.; 1.1×10^{-6} mole Cd^{++} per 200 ml.
(22) $(H^+) = 1.1 \times 10^{-2}\ M$.
(23) $(H^+) = 5.7 \times 10^{5}\ M$, impossible.
(24) $(H^+) = 1.26 \times 10^{-2}\ M$.

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(15) (a) 5.5×10^{-10}; (b) 5.4×10^{-10}; (c) 2×10^{-11}; (d) 1.5×10^{-10}; (e) 2.5×10^{-5}; (f) 1×10^{-4}; (g) 2.2×10^{-11}; (h) 4.8×10^{-11}; (i) 1.3×10^{-11}; (j) 7×10^{-10}.
(16) (*A*) *0.1 M solutions:*
(a) $7.4 \times 10^{-6}\ M$; (b) $1.3 \times 10^{-9}\ M$; (c) $1.4 \times 10^{-6}\ M$; (d) $2.6 \times 10^{-9}\ M$; (e) $6.3 \times 10^{-12}\ M$; (f) $3.2 \times 10^{-12}\ M$; (g) $4.8 \times 10^{-9}\ M$; (h) $4.6 \times 10^{-9}\ M$; (i) $1.1 \times 10^{-6}\ M$; (j) $1.2 \times 10^{-9}\ M$.
(*B*) *.01 M solutions:*
(a) $2.3 \times 10^{-6}\ M$; (b) $4.3 \times 10^{-9}\ M$; (c) $4.5 \times 10^{-7}\ M$; (d) $8.1 \times 10^{-9}\ M$; (e) $2 \times 10^{-11}\ M$; (f) $1 \times 10^{-11}\ M$; (g) $1.5 \times 10^{-8}\ M$; (h) $1.4 \times 10^{-8}\ M$; (i) $3.6 \times 10^{-7}\ M$; (j) $3.8 \times 10^{-9}\ M$.
(17) (*A*) *0.1 M solutions:*
(a) 5.13; (b) 8.89; (c) 4.75; (d) 8.58; (e) 11.19; (f) 11.50; (g) 8.17; (h) 8.34; (i) 2.96; (j) 8.92.

(*B*) *.01 M solutions:*
(a) 5.64; (b) 8.38; (c) 4.35; (d) 8.09; (e) 10.70;
(f) 11.0; (g) 7.68; (h) 7.85; (i) 2.44; (j) 8.42.

(18) (*A*) *0.1 M solutions:*
(a) 7.4×10^{-5}; (b) 7.3×10^{-5}; (c) 1.4×10^{-5};
(d) 1.2×10^{-4}; (e) 1.6×10^{-2}; (f) 3.2×10^{-2};
(g) 1.5×10^{-5}; (h) 2.2×10^{-5}; (i) 2×10^{-5};
(j) 8.5×10^{-5}.
(*B*) *.01 M solutions:*
(a) 2.3×10^{-4}; (b) 2.3×10^{-4}; (c) 4.4×10^{-5};
(d) 3.8×10^{-4}; (e) 5.2×10^{-2}; (f) 0.1;
(g) 4.7×10^{-5}; (h) 7×10^{-5}; (i) 6.3×10^{-5};
(j) 2.7×10^{-4}.

(19) 15.2 g.

(20) 9.6 g.

(21) .073 mole.

(22) 1.85×10^{-5} *M*.

(23) 2.3×10^{-5} *M*.

(24) 4×10^{-10}.

(25) Impossible — 525 *M*.

(26) (a) 2.1×10^{-4}; (b) 2.2×10^{-12}; (c) 4.6×10^{-2}.

(27) 0.33 *M*.

(28) The value of $(Fe^{++})(S^{--})$ divided by the value of $(Fe^{++})(OH^-)^2$ gives $\frac{(S^{--})}{(OH^-)^2} = 2 \times 10^{-2}$. For the FeS to precipitate first, the value of this ratio must exceed the above. For $Fe(OH)_2$ to precipitate first, the value of this ratio in the solution must be less than the above. For any solution of Na_2S this ratio can be shown to be equal to 13. Therefore, the FeS precipitates first.

(29) (a) 5.3×10^{-6} *M*; (b) 1×10^{-7} *M*; (c) .018 *M*;
(d) 4.3×10^{-9} *M*; (e) 1.6×10^{-13} *M*.

(30) $(CO_3^{--}) = 1.1 \times 10^{-4}$ *M*; $(OH^-) = 2.2 \times 10^{-6}$ *M*.

(31) $MgCO_3$. For $MgCO_3$ to precipitate first, the ratio $\frac{(CO_3^{--})}{(OH^-)^2}$ must be greater than 4.5×10^6. In this solution, the ratio has a value of 2.2×10^8.

(32) (A) *Neglecting Hydrolysis:* (a) 7.8×10^{-14} *M*; (b) 2×10^{-18} *M*;
(c) 2×10^{-13} *M*; (d) 1.3×10^{-17} *M*; (e) 2.2×10^{-11} *M*.

(*B*) *With Hydrolysis:* (a) $6.8 \times 10^{-11}\ M$; (b) $1.8 \times 10^{-15}\ M$; (c) $1.8 \times 10^{-10}\ M$; (d) $2.5 \times 10^{-15}\ M$; (e) $1.9 \times 10^{-8}\ M$.

(33) $\frac{(Ac^-)}{(HAc)} = 1.85.$

(34) $1.6 \times 10^{-6}\ M$.

(35) $\frac{(HPO_4^{--})}{(H_2PO_4^-)}$ = (a) .062; (b) 0.62; (c) 6.2.

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(11) AgCl precipitates.

(12) Yes.

(13) $2.6 \times 10^{-10}\ M$.

(14) For $Ag(CN)_2^-$, $(Ag^+) = 3.6 \times 10^{-7}\ M$.
For $Ag(NH_3)_2^+$, $(Ag^+) = 9.4 \times 10^{-9}\ M$.

(15) No.

(16) No.

(17) 1.97 g. per 100 ml.

(18) $9.1 \times 10^{-4}\ M$.

(19) $6.9 \times 10^{-7}\ M$.

(20) $1.32 \times 10^{-4}\ M$.

(21) $1.7 \times 10^{-3}\ M$.

(22) (a) $Cd(NH_3)_4Cl_2$ solution; (b) 250.

(23) $(Cu^+) = 1.9 \times 10^{-19}\ M$; $(Cd^{++}) = 9.6 \times 10^{-12}\ M$.

(24) (a) $Ag(CN)_2^-$ ion first formed; later AgCl precipitates; (b) .05 M; (c) $(Cl^-) = 0.1\ M$; $(Ag^+) = 2.8 \times 10^{-9}\ M$; $(CN^-) = 1.8 \times 10^{-6}\ M$.

(26) (b) $Fe(CN)_6^{---}$, one; $Fe(CN)_6^{----}$, none.

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(14) .034 mole.

(15) $(Zn^{++}) = 2.3 \times 10^{-6}\ M$; $(ZnO_2^{--}) = 2 \times 10^{-12}\ M$; $(H^+) = 2.2 \times 10^{-9}\ M$; $(OH^-) = 4.6 \times 10^{-6}\ M$.

(16) $(Zn^{++}) = 5 \times 10^{-13}\ M$; $(ZnO_2^{--}) = 1 \times 10^{-5}\ M$.

(17) $(Pb^{++}) = 4 \times 10^{-13}\ M$; $(HPbO_2^-) = 2 \times 10^{-3}\ M$; $(H^+) = 1 \times 10^{-13}\ M$.

(18) No.

(19) $(OH^-) = 2.5 \times 10^{-4}\ M$.

(21) $(Cu^{++}) = 1.6 \times 10^{-17}\ M$; $(HCuO_2^-) = 1.5 \times 10^{-3}\ M$; $(CuO_2^{--}) = 1.2 \times 10^{-3}\ M$.

CHAPTER 13. Pages 318–319.

(1) (a) $10^{20.4}$; (b) $10^{20.8}$; (c) $10^{-54.3}$; (d) $10^{1.2}$; (e) $10^{49.8}$; (f) $10^{84.6}$; (g) $10^{105.6}$; (h) $10^{-1.6}$; (i) $10^{-3.2}$; (j) $10^{-13.8}$; (k) $10^{21.6}$; (l) $10^{201.2}$; (m) $10^{54.8}$; (n) $10^{21.5}$; (o) 10^{77}; (p) $10^{0.8}$.

(2) Yes; $K_{eq} = 10^{140.8}$. However, in practice the stannous ion would be oxidized to the stannic ion by the nitric acid.

(3) $K_{eq} = 10^{-5.4}$; should not be dissolved appreciably.

(4) No; $(Cr^{+++})^2(Cl_2)^3 = 10^{-24}$. K_{eq} for the reaction has a value of 10^{-3}.

(5) Yes; $K_{eq} = 10^{40.2}$.

(6) No; $K_{eq} = 10^{-5.4}$.

(7) $K_I = 10^{-7.7}$.

(8) $K_{eq} = 10^{-12.2}$.

(9) Calculated $K_{eq} = 10^{7.6}$; value in Table 27 is $10^{7.9}$.

(10) $K_{eq} = 10^{11.1}$.

(11) Reaction proceeds appreciably; $K_{eq} = 10^{-2.1}$.

(12) Extremely low; (Fe^{+++}) approximately 3×10^{-24} M.

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(1) (a) 10^6; (b) 4×10^5; (c) 5×10^4; (d) 9×10^3; (e) 6×10^2; (f) 7×10^1; (g) 1.45×10^6; (h) 9.46×10^5; (i) 5.9×10^4; (j) 9.627×10^3; (k) 4.5×10^2; (l) 5.632×10^5; (m) 10^{-2}; (n) 3.2×10^{-3}; (o) 7×10^{-6}; (p) 1.07×10^{-3}; (q) 9×10^{-10}; (r) 6.78×10^{-6}; (s) 1.03×10^{-1}; (u) 1×10^{-1}; (v) 4.5×10^{-4}; (w) 6×10^{-6}.

(2) (a) 1.26×10^9; (b) 5×10^3; (c) 6.06×10^{17}; (d) 2.8×10^{-6}; (e) 5×10^{-4}; (f) 10^{-1}; (g) 7×10^4; (h) 3×10^8; (i) 6.25; (j) 1.8×10^{-7}; (k) 5×10^2.

(3) (a) 5×10; (b) 10^7; (c) $3.2 \times 10 = 32$; (d) 3×10^{-1}; (e) 4.5×10^{-5}; (f) $2 \times 10 = 20$; (g) 5×10^9; (h) 6×10^{-12}; (i) 2×10^{-12}; (j) 5×10^{-1}; (k) 3.2×10^{-1}; (l) 5×10^{13}; (m) 2×10^{-8}; (n) 5×10^{-2}.

(4) (a) 1885; (b) 16.5; (c) 16.45; (d) 3×10^{-4}; (e) $X = 10^{-4}$.

(5) (a) 3.33372; (b) 2.5315; (c) .0149; (d) $\bar{6}.826$ (or -5.174); (e) 1.8277; (f) $\bar{1}.5877$ (or $-.4123$); (g) $\bar{3}.6$ (or -2.4); (h) 2.602.

(6) (a) 4726; (b) 273.0; (c) 1.939; (d) .2226; (e) .0002905; (f) .0001861; (g) .004337; (h) .5302.

(7) (a) $V = 310$; (b) $N = 3.56 \times 10^{22}$; (c) $M = 367$; (d) $X = 3.1 \times 10^{-4}$.

(8) (a) 6.45×10^{10}; (b) 1.30×10^{-7}; (c) 1.73×10^{-9}; (d) 5.3×10^{14}; (e) 5.7×10^{14}.

(9) (a) 2×10^{-3}; (b) 4×10^{-6}; (c) 6×10^{4}; (d) 5×10^{-3}; (e) 1.58×10^{-2}; (f) 83.32; (g) 1.578×10^{-3}; (h) 1.20×10^{-7}.

(10) (a) (imaginary); (b) $+ 1.52 - 1.67$; (c) 18.5×10^{-4}, $- 19.5 \times 10^{-4}$; (d) $\pm 1.34 \times 10^{-3}$.

(11) (a) 4; (b) 11.70; (c) 5.46; (d) 7; (e) 4.59; (f) .871.

(12) (a) 10^{-7}; (b) 4×10^{-9}; (c) 5.0×10^{-6}; (d) 1.35×10^{-7}; (e) 5.62×10^{-10}; (f) 3.47×10^{-3}.

(13) (a) $P = \dfrac{K}{V}$; (b) $V = KT$; (c) $P = KT$; (d) $S = \dfrac{K}{\sqrt{m}}$;

(e) $F = \dfrac{K(m_1 \times m_2)}{d^2}$.

(14) (a) g. cm.$^{-3}$; (b) sec.$^{-1}$; (c) g. cm.^{2} sec.$^{-3}$.

(15) (g. cm.^{2} sec.$^{-3}$) does not equal (g. cm.^{2} sec.$^{-2}$).