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FUNDAMENTAL CONCEPTS OF organic Chemistry

Esmarch S. Gilreath

PROFESSOR OF CHEMISTRY
WASHINGTON AND LEE UNIVERSITY

INTERNATIONAL STUDENT EDITION

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FUNDAMENTAL CONCEPTS OF INORGANIC CHEMISTRY

INTERNATIONAL STUDENT EDITION

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Preface

This textbook is the outgrowth of several years' experience in the teaching of a course designated as *Advanced Inorganic Chemistry* at Washington and Lee University. The college catalogue describes the course as a one-semester study of special topics in the field of inorganic chemistry for advanced undergraduates. A perusal of other catalogues indicates that a similar study is offered at many other colleges and universities. One irksome task connected with the organization of teaching material has been the yearly preparation of an up-to-date syllabus to serve as a guide for student study. Furthermore the use of such a syllabus has never been quite satisfactory to me or to my students. The present volume is an attempt to remedy the problems resulting from the nonexistence of a suitable textbook.

The field of inorganic chemistry is so broad that it would be foolhardy to undertake its coverage in a single volume. Without trying to define the limits of the field, it is possible to divide this branch of chemistry into two approaches, the theoretical and the experimental, neither of which can be thoroughly explored in the duration of a single semester. This book offers only an elementary approach to certain theoretical concepts.

The choice of materials has resulted from a process of elimination. In my teaching I have used a wide range of topics, and I regret that lack of space prevents the inclusion of many of them. The ones retained are those that appear to be essential.

Despite the description of this course as a study of special topics, an examination of the table of contents will disclose that the topics are not only related but more or less dependent upon each other. The first two chapters are devoted to an analysis of the structure of matter, in the form of atomic nuclei and atomic electron shells. The third chapter is concerned with the classification of the elements, and an attempt is made to correlate the various properties of the elements and their compounds. Chapter 4 analyzes the several types of bonds which may exist among atoms, ions, and molecules and makes some prediction as to what condi-

vi · · Preface

tions are necessary for certain bond formations. Chapter 5 deals with complex ions and coordination compounds, with special emphasis upon the structural aspects of the particles concerned. The problem of solubility, and the reactions of substances in aqueous solution, make up the contents of Chap. 6. The last two chapters are surveys of two growing, and relatively new, branches of inorganic chemistry, namely, inorganic substances in nonaqueous solutions, and radioactivity and nuclear transformations.

Since this book is designed for undergraduate classroom study, a deliberate effort has been made to write it in a language suited to its purpose. Also, I have not hesitated to use elementary explanations for many controversial ideas. It is my belief that the ever-changing nature of chemistry will make many of these concepts obsolete within too short a period of time.

Many persons including various friends, colleagues, and students in chemistry have contributed to this book. It is impossible to give each of them the credit that is due. However, I do wish to express my deep appreciation to those five anonymous individuals who read the whole of the manuscript. Without their searching and helpful criticism many misstatements and ambiguities would have escaped into the final text. Also, it is a pleasant duty to express my indebtedness to my wife, Sally Gilreath, for her help in the preparation of the manuscript. Only through her encouragement and assistance was the completion of the book possible.

E. S. Gilreath

Contents

<i>Preface</i>	v
1. Atomic Nuclei	1
2. Atomic Structure ✓	70
3. Classification of the Elements	120
4. Forces between Atoms	160
5. Complex Ions and Coordination Compounds	224
6. Inorganic Reactions in Aqueous Solutions	268
7. Inorganic Substances in Nonaqueous Media	313
8. Radioactivity and Nuclear Transformations	338
<i>Index</i>	409

CHAPTER 1

Atomic Nuclei

The study of inorganic chemistry should involve some exploration into the relationships which exist among the physical properties, the chemical behavior, and the material structure of matter. Furthermore, this exploration should commence with an examination of the structure of matter, and the manner in which it is assembled. Consequently our first chapter is concerned with the particles which make up matter, and their characteristic properties. Although the building blocks of chemistry are the atoms of the several elements, these atoms are not ultimate particles of matter. To approach the possibility of fundamental particles, it is necessary to probe into the internal mechanism of the atoms themselves.

From Ernest Rutherford's experiments and speculations emerged the first modern concept of the atom. Rutherford visualized the atom as a miniature planetary system consisting of a small, heavy core, or *nucleus*, containing all of the atom's positive charge and most of its mass, surrounded by an *electron cloud* composed of negatively charged particles equal in number to the charge on the nucleus. Most of the atom's volume was conceived as empty space, patrolled by the electrons, moving in definite orbits, at relatively great distances from the nucleus and from each other.

Rutherford's picture of the atom presents two structural problems relating to the architecture of the atom. The first of these concerns the arrangement, or probability of position in space, of electrons about the nucleus, and the second pertains to the nature and arrangement of particles within the nucleus. The problem of nuclear structure will be given first consideration, inasmuch as it is in a highly speculative stage of development and, consequently, can be disposed of more quickly.

SUBATOMIC PARTICLES

The idea that matter is constructed of ultimately indivisible particles is as old as natural philosophy. From the Greeks came the beginning of the atomic theory; Democritus taught that atoms are hard, small

2 Fundamental Concepts of Inorganic Chemistry

objects—so small as to render them invisible—with form, size, and weight. This old atomic hypothesis was placed on a useful scientific basis by John Dalton, who in 1803 developed the concept of atomic weights. Dalton's atomic theory contained the famous postulate that atoms of the same elements are similar to one another and equal in weight. This led Prout, an Edinburgh physician, to suggest in 1815 that all atoms are made of the same primordial atoms of a substance which he called "protyle" and which he attempted to identify as hydrogen. However, Prout's hypothesis was short-lived since accurate atomic-weight determinations by Berzelius and by Stas proved that atomic weights of many elements were not integral multiples of the weight of the hydrogen atom. Despite this early deathblow to the Prout hypothesis the idea of an ultimate particle or particles has lingered in the minds of physicists and chemists since its inception. Even at present there is much speculation among top-flight scientists that the composition of matter may yet be resolved into a few fundamental particles.

1.1 The Enigma of Fundamental Particles. The problem of breaking the atom down into its component particles has progressed from what appeared at first to be a simple, logical solution involving only three fundamental particles, namely, electrons, protons, and neutrons, into an entangled, obscure situation, embodying a multiplicity of particles. The known and probable particles coming from the atom total at least 20, with others likely to be added before some resolution is made of the present number. In the analysis of mass particles it is also necessary to account for particles of energy; however, the border line between mass and energy is not always clear-cut. Despite the fact that twenty or more particles have been observed as products of nuclear reactions of various types, this does not necessarily mean that the nucleus is a mixture of these particles. It is unlikely, for example, that photons are constituent particles. Photons, which are units of high-frequency electromagnetic radiation, e.g., gamma rays, may result from internal stresses within the nucleus, in which mass is converted into energy. It is also quite possible that mass particles such as electrons, positrons, and mesons do not exist as components but are created by stresses in which energy is converted into mass. It is much easier to return to an earlier hypothesis in which the nucleus is considered as being composed of two building blocks, protons and neutrons, which are collectively called nucleons. Perhaps all the other particles coming from the nucleus are by-products created by interaction of the two types of nucleons. Various theories as to the structure of the nucleus will be discussed in more detail later in this chapter.

No particles are necessarily immutable, and therefore none can be considered as truly fundamental. All the known particles existing in nature

have been found to undergo various types of reactions, either with other particles and radiation or by decay. For the purpose of this study we shall classify particles existing outside the atom into two types: those which are stable, and those which are unstable. The term *stable*, or *stability*, denotes an absence of decay but does not necessarily imply long life; e.g., the positron is a stable particle, but usually short-lived because it is rapidly destroyed by interaction with an electron.

Before listing and describing the various stable and unstable particles which are believed to be fundamental, it seems pertinent to examine certain general properties which are more or less common to all particles.

1-2 Properties of Nuclear Particles. The most important properties of nuclear particles are their charge, mass, and spin. One or more of these properties may be absent in a given particle; e.g., the neutron has zero charge, the neutrino has zero mass, and the various mesons are supposed to have zero spins. Certain conventions have been adopted for indicating as many of these properties as possible in the symbolic representations of the particles. First of all, each particle has an identifying abbreviation or symbol; these are listed in Tables 1-1 and 1-2. The charge, if any, is shown as a subscript to the symbol of the particle, and the mass, to the nearest whole number, is written as a superscript. Thus the correct representation for the neutron is n^1 , indicating that this particle has zero charge and a mass number of 1. The alpha particle, although not considered as a fundamental nuclear particle, may be used as another illustration. This nuclear fragment is written as ${}_2\text{He}^4$, signifying that it is a helium nucleus, with a charge of $+2$ and a mass of 4. Still another illustration is that for the electron, ${}_{-1}e^0$, which denotes the particle as having zero mass and a charge of -1 .

The mass of nuclear particles may be described by either of two systems. One system is based on the unit of the physical atomic-weight scale. In this system the unit of mass, frequently referred to as *mass unit*, is one-sixteenth the mass of the ${}_{8}\text{O}^{16}$ atom of oxygen. In other words, the unit of mass is one-sixteenth the atomic mass of the O^{16} isotope of oxygen. This particular isotope has been selected as the standard for the physical atomic-weight scale, and the unit of this scale is usually designated as amu (atomic mass unit). A discussion of isotopes and the physical atomic-weight scale is given later in this chapter in Secs. 1-18 and 1-16.

(Another system of designating mass for nuclear particles is based on the charge of the electron. The apparent mass of an electron depends upon the speed with which it is traveling. For an electron moving with small velocity the ratio of the charge to mass, e/m , is 5.274×10^{17} esu (electrostatic units)/g. Since the charge of the electron, e , has been determined as 4.803×10^{-10} esu, the mass may be calculated as

4 Fundamental Concepts of Inorganic Chemistry

$$m = \frac{4.803 \times 10^{-10}}{5.274 \times 10^{17}} = 9.107 \times 10^{-28} \text{ g}$$

The value $9.107 \times 10^{-28} \text{ g}$ is referred to as the *rest mass* of the electron, and if this value is arbitrarily designated as unity, then the masses of other particles may be assigned values relative to that of the electron. To illustrate, the mass of the proton, on this scale, is 1,836.14, indicating that this particle has a mass over 1,800 times greater than that of the electron.

In Tables 1.1 and 1.2 the masses of known particles are listed in the units of both the systems just described.

All bodies in space—the sun, the earth, and even nuclear particles—manifest the property of angular momentum, usually called *spin*. For simplicity it is easier to think of a particle as spinning like a top around its own axis; however, physicists usually prefer to think of spin as a mathematical notation rather than an actual physical rotation. This property can be measured, and the unit of spin is Planck's constant, h , divided by 2π . Since the laws of quantum mechanics require that the spin of any particle or system of particles be quantized, the value of the spin is always an integral or half-integral multiple of $h/2\pi$. Most fundamental particles, such as an electron or a proton, have spins in units of $+\frac{1}{2}$ or $-\frac{1}{2}$. The combination of the spins of these or other fundamental particles in an atomic nucleus results in systems with spins of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, etc., but never in intermediate values such as $\frac{3}{4}$. When the atomic weight of an atom is an even number, the number of particles in the nucleus will also be even in number and the nuclear spin will be zero or a whole number, usually 1.

The spin numbers of all particles in a nuclear reaction must be balanced on both sides of the nuclear equation. This provides a convincing argument for postulating the neutrino particle, which is needed to balance the nuclear equation when an electron is emitted from a radioactive nucleus in beta decay. The need for postulating this hypothetical particle is described in the next section.

1.3 Stable Particles. Four mass particles and three energy particles have been either identified or postulated which are not subject to decay. The mass particles are the electron, the proton, the antiproton, and the positron; the energy particles are the neutrino, the photon, and the graviton. The general characteristics of these particles are summarized in Table 1.1.

The Electron. This was the first particle to be recognized as a constituent of all atoms. The first evidence of its existence dates back to Michael Faraday, who, in 1833, while studying the conduction of electricity by solutions, reached the conclusion that a flow of electricity was due to a movement of discrete particles. In 1879 Sir William Crookes

showed that cathode rays could be bent by an electromagnetic field, indicating that cathode rays are particles of matter. In 1895 Jean Perrin showed that the charge on these particles is negative. As early as 1874 G. Johnston Stoney had recognized the need for the particle, and after its discovery it was he who suggested the name *electron* for this unit of matter. It was in 1897 that Sir J. J. Thomson assigned the first value for the ratio of the charge of the electron to its mass. By observing the deflections of cathode rays in magnetic and electrical fields of known strengths he was able to determine the velocities of the particles and the ratio of their charge e to their mass m . The value he obtained for e/m was 1.77×10^7 emu (electromagnetic units)/g, which was far from the correct value as shown by more precise measurements in subsequent determinations. However, the true importance of his work lay in his observation that the value of e/m was independent of the metal used as the cathode and the nature of the gas in the tube, indicating that the nature of the particles from various metallic cathodes was the same.

The history of the identification of the electron, and the determination of its properties, is replete with the famous names of science; however, it is not proposed to reproduce this history here. It will suffice to note a few of the most important constants which have been determined for the electron.

Its charge e is 4.8024×10^{-10} esu, or about 1.60×10^{-19} coulomb. The most reliable measurements of e/m for the electron, at low velocity, is 5.274×10^{17} esu. Its mass is 9.106×10^{-28} g, 1,836 times less than the proton, or 0.0005486 on the physical scale of isotopic weight. (This scale is designated in Sec. 1-4 and described in Sec. 1-16.)

The Proton. The discovery of the electron stimulated a search for the corresponding unit of positive charge. In 1886 Eugene Goldstein, using a perforated metal disk as a cathode, in a cathode-ray tube, observed luminous rays emerging in straight lines from the holes in the disk and moving in a direction opposite to the cathode rays. In 1898 W. Wien showed that these rays were deflected in a magnetic and in an electric field, but in opposite direction to the deflection of electrons in the same fields, indicating that they were streams of positively charged particles. The rays were originally called *canal rays* since they passed through channels in the cathode, but in 1907 J. J. Thomson proposed the more appropriate name of *positive rays*. A determination of the ratio of charge to mass, e/m , of the particles making up the positive rays showed that they were much heavier than electrons. The lightest of these particles had a mass approximately that of the hydrogen atom; consequently it was assumed that such a particle was merely a hydrogen (protium) atom stripped of its lone electron. The name *proton*, coming from the Greek word for *first*, was suggested for it by Sir Ernest Rutherford in 1920.

6 Fundamental Concepts of Inorganic Chemistry

The mass of the proton in the free state, as determined from mass spectrum measurements, is 1.007581 on the physical scale, or 1.6725×10^{-24} g.

The Positron. Up to 1932 the only unit of positive charge recognized was the hydrogen positive ray of mass 1, which is the hydrogen nucleus, or hydrogen ion. However, in 1930, the existence of positive electrons, as distinct from protons, was predicted theoretically by Paul A. M. Dirac, the English mathematical physicist, on the basis of his relativistic quantum theory of the electron. Proof of the existence of the positive electron, now called the *positron*, was obtained by Carl D. Anderson, an American physicist, during his study of cosmic rays. From its path in a cloud chamber Anderson proved the positive charge of the positron. When this particle passes through a lead plate, it loses some of its energy and this loss of energy affects the degree of curvature in a magnetic field and the intensity of the track itself. Thus measurements made on the track of a particle before and after it had passed through a lead plate enabled Anderson to evaluate the mass of the particle and the magnitude of its electric charge.

The Antiproton. For many years theoretical physicists have speculated upon the probable existence in nature of particles as pairs possessing similar but opposite characteristics. This concept is sometimes termed the *electric-charge symmetry in nature* and predicts that for each fundamental mass particle occurring in nature there should exist a similar particle of opposite electrical charge. The occurrence and characteristics of the electron-positron pair illustrates the idea embodied in this concept. Furthermore physicists have predicted that comparable symmetry may exist in other characteristics. According to the broader theory, not only should a negatively charged proton, called an *antiproton*, exist, but there should also occur in nature a symmetrical companion to the uncharged neutron, called the *antineutron*. Such a theory would also predict the probable existence of the *antineutrino*.

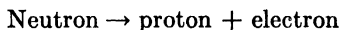
The concept of electric-charge symmetry predicted the possible existence of the antiproton, with a mass equal to the proton, but with a negative charge. Such a particle could not be expected to exist free in nature because it would be annihilated rapidly upon contact with other matter. In fact its existence is possible only at a distance from the earth's crust and atmosphere or momentarily as a newly created particle in a powerful proton accelerator.

In 1955 the existence of the antiproton was confirmed by scientists at the Universities of California and of Rome. The creation of the antiproton was accomplished at the University of California by means of a powerful proton synchrotron called a *Bevatron*. This accelerator, as the name implies, is capable of accelerations above a billion electron volts

(Bev). In the Bevatron chamber protons accelerated to 6.2 Bev were directed upon a copper target. When a proton with this acceleration hits a neutron in a copper atom, two new particles are produced—a proton and an antiproton. In such a collision a part of the proton's energy is converted to mass in accordance with Einstein's equation, and the remaining energy produces motion in all particles remaining or created by the collision. In this experiment nearly 1 Bev of the original 6.2 was required to create each antiproton.

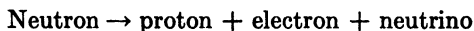
The mass of the antiproton is equal to that of the proton. It is stable in a vacuum and does not decay spontaneously; however, as has been said before, it is annihilated upon contact with either neutrons or protons. The particle bears a negative charge and has a spin of $\frac{1}{2}h$. These characteristics are listed in Table 1-1.

The Neutrino. The emission of an electron from a radioactive (unstable) nucleus, called *beta decay*, is evidently due to the transformation of a neutron into a proton and an electron.



In beta decomposition the energy of the neutron should be equal to the energy of the products, but it has been found that the beta particles (electrons) which are emitted have a range of values of kinetic energy. This would appear to be a contradiction of the law of conservation of energy. In the same process another conservation principle, the law of conservation of angular momentum, seems to have been violated. In Sec. 1-2 it was stated that the spins of fundamental particles, such as neutrons, protons, and electrons, are either $+\frac{1}{2}h$ or $-\frac{1}{2}h$. In this transformation the neutron with a spin of $\pm\frac{1}{2}h$ gives rise to two particles, the proton and the electron, each with a spin of $\pm\frac{1}{2}h$. Since the spin numbers must be balanced on both sides of the equation for the nuclear reaction, an extra $\frac{1}{2}$ -spin unit must be accounted for. Either a $\frac{1}{2}$ -spin unit is gained in the production of two new particles, or, if there is a balancing of opposite spins, there is a loss of a $\frac{1}{2}$ -spin unit.

The *neutrino* was a theoretical particle postulated by Wolfgang Pauli in 1931 to preserve the conservation of energy and angular momentum in beta decay. With the addition of this new particle the creation of an electron in the nucleus could be represented as



in which the proton is retained in the nucleus and two particles, the electron and the neutrino, are emitted. Assuming the neutrino has a spin of $\pm\frac{1}{2}h$, the unbalanced angular momentum is restored, inasmuch as the neutron with a half-integral spin is transformed into three particles, the sum of whose spins is a half-integral.

8 Fundamental Concepts of Inorganic Chemistry

Existence of the free neutrino was established experimentally in 1956 by a group of Los Alamos scientists working with a complex detecting system set up near a powerful reactor at the Savannah River plant of the Atomic Energy Commission. The late discovery of the neutrino particle may be attributed to the fact that its charge is zero and its mass is either zero or very close to zero. Some physicists postulate the existence of an antineutrino to distinguish between β^- and β^+ decay. However, there appears to be no definable difference between the two particles.

The Photon. It is fairly easy to think of matter as composed of fundamental particles, but it requires considerable imagination to visualize

TABLE 1-1 CHARACTERISTICS OF CERTAIN STABLE ELEMENTARY PARTICLES

Particle	Symbol	Charge	Mass*	Mass†	Spin‡
Electron.....	e, β^-	—	0.0005486	1	$\frac{1}{2}$
Proton... ..	p	+	1.00758	1,836	$\frac{1}{2}$
Positron... ..	e^+, β^+	+	0.0005486	1	$\frac{1}{2}$
Neutrino... ..	ν	0	<0.00002	<0.04	$\frac{1}{2}$
Photon... ..	γ	0	0	0	1
Graviton... ..	G	0	0	0	2
Antiproton... ..	$\bar{p}$	—	1.00758	1,836	$\frac{1}{2}$

* The unit is the physical atomic weight; ${}_8\text{O}^{16} = 16.00000$.

† Mass relative to e , where $e = 9.11 \times 10^{-28}$ g.

‡ In units of $\hbar/2\pi$.

energy as made up of ultimate particles. However, according to the quantum theory, energy, as well as matter, is made up of discrete units. The photon is the unit of electromagnetic radiation. The history of the photon goes back to Max Planck, who in 1901 pointed out that the distribution of energy in black-body radiation could not be reconciled with the wave theory of light and suggested the hypothesis that energy is emitted or absorbed discontinuously in multiples of a certain unit, or *quantum*. Furthermore, the magnitude of this unit, or quantum, is $h\nu$, where ν is the frequency of the radiation and h is a constant, which has become known as *Planck's constant*.

In 1905 Albert Einstein suggested that not only was radiation absorbed and emitted in whole numbers of energy quanta but that it was also propagated through space in definite quanta, moving with the speed of light. The term *photon*, coming from the Greek word for *light*, was introduced in 1928 by A. H. Compton. Earlier, in 1923, Compton had discovered (Sec. 2-12) that, when X rays fall on any material of low atomic weight, the scattered rays consisted of two frequencies, one equal to and the other less than that of the primary rays. To account for the

change in frequency in the scattered rays, Compton deduced mathematical equations which accounted perfectly for this frequency change in terms of body collisions. According to these equations the frequency change is due to the collision of an X-ray photon with an electron in the material on which it impinges, producing, in the recoil, another photon (the scattered X ray) of longer wavelength.

The Graviton. The elementary particle corresponding to the gravitational field, more aptly described as the *unit of gravitational energy*, is the *graviton*. This particle has never been observed, but the postulation of its existence is necessary in certain mathematical equations relating to quantum mechanics. Gravitational forces are extremely weak, the weakest of all the physical forces, and, for this reason, gravitational effects are observed only in large masses. In such masses the number of gravitons must be quite large, but since the particle itself is postulated as having zero mass and zero charge, it is doubtful that the individual graviton will ever be observed.

1.4 Unstable Particles. Any estimate as to the number of unstable elementary particles that may exist would be an extremely unsafe guess, inasmuch as new particles are being discovered at a rate somewhat discomforting to most scientists. This discomfort arises not from the actual discoveries of the new particles but from the fact that the problem of nuclear structure is increasing in complexity, with any possible solution being pushed further into the future. Not only is there the problem of new additions to the number of known particles, but the fact that so many change from one type to another is quite disconcerting.

Among the unstable elementary particles that will be described are the *neutron*, the family of particles known as *mesons*, and the $\bar{V}$ particles. The general characteristics of these particles are summarized in Tables 1.2 and 1.3.

The Neutron. Of all the particles that have been, or will be, discussed, the neutron is the most intriguing. Our knowledge of the properties and behavior of the neutron is extensive; our lack of knowledge of the role it plays within the nucleus is abysmal. Undoubtedly it is one of the fundamental building blocks of nature, and for that reason we shall cite all its known properties and shall later explore some of the speculative theories as to its function in the nucleus.

Atoms of the same element may vary in their atomic masses. Among the most popular of the earlier explanations for this variation was the theory that the nucleus consisted of protons and electrons and that weight differences in atoms were due to different numbers of proton-electron combinations in the nucleus. However, theoretical difficulties of dealing with electrons as nuclear building stones led to the prediction by Sir

10 Fundamental Concepts of Inorganic Chemistry

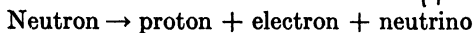
Ernest Rutherford, in his Bakerian Lecture to the Royal Society in 1920, of the existence in the nucleus of a neutral, uncharged particle, having a mass of unity on the atomic-weight scale.

The brilliant prediction of Rutherford remained unverified for 12 years. Among the first attempts to produce such particles was the passage of an electric discharge through hydrogen, with the hope of causing the union of electrons with protons, but experiments of this nature were unsuccessful. In 1930 Bothe and Becker of Germany bombarded targets of lithium, beryllium, and boron with alpha particles from the natural radioactive element polonium and found that an uncharged radiation with an unusually high penetrating power was produced. These results were confirmed in 1931 by Frédéric Joliot and Irène Joliot-Curie in France. The Joliot's made the additional observation that, when a screen of paraffin was interposed in the path of the new radiation, high-speed protons were ejected. This effect might possibly be produced by gamma rays of very short wavelength, and for some time this explanation was accepted. Finally, in 1932, James Chadwick of Cambridge University repeated these experiments, using beryllium as a target for the alpha particles, but directed the new radiation into a Wilson cloud chamber filled with nitrogen. The ionization produced in the chamber was measured and then the experiment repeated with a sheet of paraffin in the path of the secondary radiation, before its entrance into the cloud chamber. The interposition of the paraffin sheet increased considerably the ionization within the cloud chamber. Such an increase was due to protons produced in the paraffin by the secondary radiation from the beryllium. Moreover the production of protons was little affected by placing a lead screen between the beryllium source and the paraffin. The events in the cloud chamber could be interpreted only as body collisions of particles too massive to be caused by weightless gamma radiation. The approximate mass of the new particles emanating from the beryllium target was determined by Chadwick through a comparison of the maximum velocities of protons and nitrogen nuclei produced by the impacts of the new particles in hydrogen and nitrogen, respectively. The new particles were called *neutrons* since they were electrically neutral, and consequently their paths were not visible in a cloud chamber. Despite the foregoing statements concerning the behavior of neutrons in a cloud chamber they produce no primary ionization but may be detected by the fact that in collisions with charged nuclei (nitrogen atoms, in this case) they will impart energy to them, and these secondary moving nuclei will ionize and be detectable.

† The specific properties of the neutron may be listed as: zero electric charge, a mass of 1.00893 on the physical atomic-weight scale, and a spin of $\frac{1}{2}$. It has a half life of approximately 20 min, undergoing spon-

taneous destruction, with the formation of a proton, an electron, and a neutrino according to the equation

C. A. Appleton.



This is the reaction that was postulated as taking place in beta decay (Sec. 1-3), making necessary the invention of the neutrino particle, even before its discovery, to preserve the conservation of angular momentum. Direct experimental proof for this decay has been obtained only recently owing to the fact that free neutrons are captured so rapidly by nuclei that the average life of a free neutron is short in comparison with its expected radioactive half-life period.

The neutron has zero electric charge, but the statement that it is a neutral particle should have some qualification. It is true that no deflection can be observed in the slowest of neutrons with the strongest electric fields. Also true is the fact that the neutron, in itself, causes no ionization in a cloud chamber. On the other hand the neutron has magnetic properties which seem contrary to what might be expected of a totally neutral particle. A neutron will align itself in the fashion of a small magnet when placed in a magnetic field. It has also been observed that slow neutrons are deflected from their course by passing them through magnetized iron. Moreover the electrically neutral neutron possesses a magnetic moment equivalent to that of a spinning negative charge. As might be expected, the magnetic moment of the neutron is negative and opposite in sign to the magnetic moment of the proton, which is a spinning positive charge.

The magnetic moment of the neutron would indicate that it possesses some type of charge-bearing structure, although it is neutral over-all. Recent experiments have explored this possibility, and there seems a likelihood that the neutron consists of a positively charged core surrounded by a thin shell containing an equal quantity of negative charge. In fact there is some experimental evidence that neutrons may interact slightly with electrons—a behavior quite contrary to what would be expected of a neutral particle.

Mesons. From the time of the discovery of the neutron in 1932, scientists have felt that the essential building blocks of the nucleus are neutrons and protons. Beginning with that date, they have struggled to assemble some sort of theory to explain the extremely powerful forces that are necessary to hold together these heavy particles in the very small nucleus. Theorizing along this line led the Japanese physicist Hideki Yukawa to suggest in 1935 that a kind of field, consisting of quanta of energy which could take the form of particles of a certain mass, might account for the nuclear binding forces. Although the speculative theories regarding nuclear structure will be given in more detail later in this

12 Fundamental Concepts of Inorganic Chemistry

chapter, it is interesting to note that the existence of a new particle, or particles, was postulated from an analysis of exchange forces between a proton and a neutron. Yukawa assumed the effective range of nuclear forces to be 2.8×10^{-13} cm and the approximate distance between centers of adjacent particles within the nucleus to be of the same magnitude. By equating this distance to $h/2\pi mc$, a formula which relates mass to the field quantum exchanged between two particles, he estimated the mass of the field quanta exchanged between the proton and neutron to be about 200 times the mass of the electron. These exchange particles later became known as *mesotrons* and *mesons*.

If it is assumed that there are only two fundamental nucleons, protons and neutrons, three types of bonds may be envisaged within the nucleus, i.e., proton-neutron, proton-proton, and neutron-neutron. Furthermore, since one of these nucleons bears a charge and the other does not, it may be further assumed that three kinds of exchange particles, or mesons, are necessary for nuclear binding: one being positive, another negative, and the other neutral.

When Yukawa propounded his theory, no such particles were known. Scientists do not care to invent unobservable, imaginary particles. The only justification for the invention of such a particle is for the purpose of explaining an observed reaction in such a manner that a conservation principle will not be violated. It will be recalled that this argument justified the invention of the neutrino. The absence of a similar necessity would probably have relegated Yukawa's theory to obscurity had it not been that particles with masses of this order were discovered soon after the theory was proposed.

Within 2 years after the publication of Yukawa's meson theory containing the prediction of nuclear particles intermediate in mass between an electron and a proton, and with a calculated mean life of about 10^{-6} sec, physicists found in cosmic radiation a particle which seemed to have just the properties that Yukawa had predicted. During the years 1936 and 1937 Carl D. Anderson and Seth H. Neddermeyer at the California Institute of Technology and J. C. Street and E. C. Stevenson at Harvard University found charged particles, both positive and negative, in atomic debris produced by cosmic rays. These particles had a mass approximately 200 times that of an electron.

The disheartening anticlimax to the meson story was the failure of these newly discovered particles to react with nucleons. Although mesons were found to be produced with ease by cosmic radiation and possessed the characteristics predicted by Yukawa, they were rarely absorbed by nuclei of atoms. This lack of nuclei capture indicated one important fact, namely, that the interactions between mesons and nucleons were too weak for the former to serve as a source of the forces holding nuclei together.

Ten discouraging years passed for nuclear physicists, especially those interested in the meson theory of nuclear forces. Finally it was suggested that perhaps there were two types of mesons: (1) a heavier species, possessing the properties Yukawa had proposed, and responsible for holding nucleons together; and (2) a lighter species resulting from the decay of the heavier type. According to this two-variety-meson theory the heavier mesons are produced by cosmic radiation in the upper atmosphere and decay too rapidly to penetrate very far into the atmosphere. The lighter mesons are produced by the decay of the heavier variety and are the ones that scientists had been observing for ten years. In 1947 C. F. Powell, G. P. S. Occhialini, and C. M. G. Lattes, working high in the Bolivian Andes, discovered a meson which did interact strongly with nucleons. This meson has a mass 276 times greater than that of an electron and appeared in every way to be identical with Yukawa's meson. The symbol π was chosen for this heavier meson by Powell and his collaborators to designate the word primary, since pi mesons are primary products of the interaction of cosmic rays with nuclei. The symbol μ was selected to represent the lighter mesons. The pi mesons are at present frequently designated as *pions* and the mu mesons as *muons*.

The pi mesons exist in three forms: the positive pi meson, the negative pi meson, and the neutral pi meson. It will be recalled that Yukawa postulated the existence of three such particles to account for the three types of bonds within the nucleus. The charged pions have a mass of 276 times that of the electron. The neutral pion is slightly lighter, with a mass of 265—as yet this difference in mass has not been fully explained. The spin of the pions is zero. The charged variety of pions undergo spontaneous destruction, with half life of 2.6×10^{-8} sec, into mu mesons, of like charge, and photons. The neutral pion has a much shorter half life, about 10^{-16} sec, and is destroyed by spontaneous decomposition into two photons. The decay reactions of the pions are given in Table 1-3.

Only the positively and negatively charged forms of the mu mesons have been found. This lack of discovery does not exclude the possibility of the existence of a neutral muon, since such a particle would be quite elusive; nevertheless it should be noted that the decay schemes for the pions do not indicate the production of a neutral muon. The spin of the mu mesons is $\frac{1}{2}h$. The mass of the muons has been determined as 210 times that of the electron. They spontaneously decompose with a half life of 2.1×10^{-6} sec. The positive muon decomposes into a positron and two neutrinos, whereas the negative muon breaks down into an electron and two neutrinos. The decay schemes for these particles are given in Table 1-3.

Since the discovery of the pions, heavier mesons have been found but it is doubtful that they are important in the interpretation of nuclear forces. Five of these heavier varieties are listed in Tables 1-2 and 1-3.

14 Fundamental Concepts of Inorganic Chemistry

TABLE 1-2 CHARACTERISTICS OF CERTAIN UNSTABLE ELEMENTARY PARTICLES

Particle	Symbol	Charge	Mass*	Mass†	Spin‡
Neutron.....	n	0	1.00893	1,838 5	$\frac{1}{2}$
Positive mu meson.	μ^+	+	0.1152	210	$\frac{1}{2}$
Negative mu meson	μ^-	-	0.1152	210	$\frac{1}{2}$
Neutral pi meson...	π^0	0	0.1454	265	0
Positive pi meson...	π^+	+	0.1514	276	0
Negative pi meson	π^-	-	0.1514	276	0
Zeta meson ?.....	ζ	$\pm$	0.3018	550	?
Tau meson.....	τ	$\pm$	0.5349	975	?
Kappa meson.	κ	$\pm$	0.6035	1,100	?
Positive chi meson.	χ^+	+	0.7680	1,400	?
Negative chi meson.. . . .	χ^-	-	0.7680	1,400	?
Neutral V particle.. . . .	V_1^0	0	1.2014	2,190	?
Neutral V particle.. . . .	V_2^0	0	0.4643	850	?
Negative V particle	V^-	-	1.2069	2,200	?
Positive V particle.....	V^+	+	1.2069	2,200	?

* The unit is the physical atomic weight, in which $^{16}\text{O} = 16.00000$.

† Mass relative to e , where $e = 9.11 \times 10^{-28}$ g.

‡ In units of $\hbar/2\pi$.

TABLE 1-3 DECAY SCHEME OF CERTAIN UNSTABLE ELEMENTARY PARTICLES

Particle	Half life, sec	Mode of decay
Neutron.....	750	$n \rightarrow p + e + \bar{\nu}$
Positive mu meson.	2.1×10^{-6}	$\mu^+ \rightarrow p + 2\nu$
Negative mu meson.	2.1×10^{-6}	$\mu^- \rightarrow e + 2\nu$
Neutral pi meson...	10^{-18}	$\pi^0 \rightarrow 2\gamma$
Positive pi meson...	2.6×10^{-8}	$\pi^+ \rightarrow \mu^+ + \nu$
Negative pi meson...	2.6×10^{-8}	$\pi^- \rightarrow \mu^- + \nu$
Zeta meson ?.....	10^{-12}	$\zeta \rightarrow \pi + ?$
Tau meson....	10^{-8}	$\tau \rightarrow 3\pi$
Kappa meson.. . . .	?	$K \rightarrow \mu + ?$
Positive chi meson.	10^{-9}	$\chi^+ \rightarrow \pi^+ + ?$
Negative chi meson.	10^{-9}	$\chi^- \rightarrow \pi^- + ?$
Neutral V_1 particle.	3×10^{-10}	$V_1^0 \rightarrow p + \pi^-$
Neutral V_2 particle.	10^{-10}	$V_2^0 \rightarrow \pi^+ + \pi^- + ?$
Negative V particle.	10^{-10}	$V^- \rightarrow n + \pi^- + \pi^0$
Positive V particle.	10^{-10}	$V^+ \rightarrow p + \pi^- + \pi^0$

V Particles. The V particles were first observed in a cloud chamber by G. D. Rochester and C. C. Butler of England in 1948 during the course of a cosmic-ray investigation. A positive V particle, a negative V particle, and two varieties of a neutral V particle have been reported; however, there is some doubt about the existence of the positive V

particle. The negative and one of the neutral V particles have a mass about 2,200 times that of the electron; the other neutral V particle has a mass of approximately 850. These particles are quite unstable, decaying into simpler products, although the identities of the decay products are as yet in doubt. It is probable that the heavier varieties break down into mesons, most likely pions, and the lighter V particle may decay into muons. Speculative decay reactions for these particles are given in Table 1-3.

THE STRUCTURE OF THE NUCLEUS

During the discussion of subatomic particles it was frequently necessary to make certain allusions to nuclear structure. These indirect references were to be expected, since the discovery of fundamental units of matter resulted almost wholly from a search for information which might lead to a satisfactory explanation of nuclear structure. Moreover this search has been most intense. It has been said that during the past quarter of a century more man-hours have been devoted to the problem of what holds the nucleus together than have been given to any other scientific question in the history of mankind. We might also add that those man-hours of labor and thought have not been so fruitful as one might have hoped. Consequently, though our past references to the structure of the nucleus have been fragmentary, even when we bring these fragments together and add to them all other information that is available, the picture is still far from complete.

1-5 Nuclear Forces. The forces that bind the nucleus together are very great, at least millions of times greater than those which bind atoms together in a molecule. Forces of this magnitude are alien to man's experience. Accustomed-as he is to the pull of gravity, and to the observation of electrical attraction or repulsion between charged bodies, he must now condition his thinking to forces which dwarf these by comparison. For instance, two protons at a nuclear distance from each other undergo an electrostatic repulsion of about 6 tons, but the *nuclear forces* attracting the same two particles are at least 40 times as great. On the other hand gravitational forces between the two protons can be considered as negligible as compared with either electrostatic or nuclear forces. From this illustration it may be deduced that the two major forces in the nucleus are electrostatic and nuclear, of which the latter is by far the stronger.

It is a logical assumption that the nucleus is made up of particles. If this be true, then it must also be concluded that there is space between the individual units of nuclear matter. Again the imagination of man must be strained beyond the limitations of his ordinary conceptions, and

16 Fundamental Concepts of Inorganic Chemistry

this time in regard to space. The density of nuclear matter is 130 million tons/cc, or about 100 trillion times that of water. Space and distance between particles in matter so dense must be small indeed. Another unusual feature of nuclear matter is the fact that all nuclei have a uniform density. In other words, the density of nuclei does not vary from atom to atom but is a constant quantity.

Coulombic and gravitational forces, with which man is familiar, are long-range forces operating over relatively long distances. Furthermore the strength of these forces is approximately proportional to the square of the masses or charges of the bodies involved. The well-known laws followed by these familiar forces do not apply to nuclear forces. Thus the force between two nuclear particles apparently depends upon distance (but not in the same relation as in other forces), upon their velocities, and upon their spins. It is practically independent of the particles' charge. In the case of multiple particles the force is not proportional to the square of the number of particles but is approximately proportional to the number of particles. Experimental facts lead strongly to the belief that nuclear forces of attraction have a saturation value, somewhat analogous to the binding forces between atoms in a molecule. For example, two hydrogen atoms attract each other strongly to form a hydrogen molecule, H_2 , and then attract no additional atoms. In like manner it is believed that two protons and two neutrons tend to unite into an alpha particle to form a saturated system.

Calculations show that the radius of an atomic nucleus is of the order of 10^{-13} to 10^{-12} cm, which, surprisingly enough, is about the size of an electron. This extremely small size, coupled with the immense density of the nucleus, indicates that nuclear forces would be short-range forces, operating over very short distances only. Experimental evidence has verified this prediction. If high-speed protons are projected at hydrogen nuclei (also protons), it has been found that the electric force of repulsion, which amounts to about 6 tons for each two particles, is overcome when the projectile proton reaches within 10^{-13} cm of the target proton. Moreover the nuclear force of attraction which goes into action at this distance is 40 times greater than the force of repulsion, and 10^{37} times greater than the gravitational force between the two protons. Also, as predicted, the nuclear force operates over a short range only. If it is assumed that the nuclear force of attraction between two protons is at a maximum at 1×10^{-13} cm, an increase in distance of 4 times, or to 4×10^{-13} cm, causes the nuclear force to drop in strength until it is no greater than that of the coulombic force of repulsion. In other words, the magnitude of the nuclear force will drop 40 times in separating the two particles by a distance of 0.0000000000004 cm. Furthermore, if the distance between protons is increased 25 times, the coulombic repulsion will

become 1 million times greater than the nuclear force of attraction. To add to the complexity of the analysis of nuclear forces, if the distance of maximum force intensity between particles is decreased appreciably, the tremendous force of attraction is converted into an even greater force of repulsion. In other words, the density of nuclear matter cannot be increased without causing its disintegration.

1-6 Electron-Proton Concept. Any theory of the structure of the nucleus must account not only for the mass of the nucleus but also for its charge. The nucleus contains about 99.95 per cent of the total mass of the atom, and a positive charge equivalent to the number of electrons surrounding it. Prior to 1932, the date of the discovery of the neutron, it was generally believed that nuclei were composed of protons and electrons. In this early model ⁴He nucleus was considered to contain sufficient protons to account for its approximate mass, each proton having a mass equal to one unit of atomic weight, and sufficient electrons to reduce the net positive charge to a value equivalent to the number of planetary electrons. Thus, if an element of atomic weight A had an atomic number Z (see Sec. 2-4 for an explanation of the term *atomic number*), its nucleus would contain A protons and $A-Z$ electrons. According to this early theory the total number of electrons, whether nuclear or extra-nuclear, contributed a negligible amount to the total mass. Furthermore the nuclear particles, electrons and protons, were viewed as separate particles and not as fusion particles of the two charged units. One strong argument in favor of the earlier model was the emission of beta particles (electrons) by certain radioactive elements which were presumed to come from, and be constituents of, the nucleus.

This theory failed to permit any quantitative conclusions as to the behavior of electrons in the nucleus. For example, as was stated in the previous section, the size of an electron is approximately the same as that of the average nucleus; therefore it was obviously impossible to pack so many large particles into a single body of the size of one electron. Another quantitative difficulty occurred in an attempt to evaluate the angular momenta of nuclei. As was explained in Sec. 1-4, the total angular momentum of a nucleus may be accounted for by adding up the angular momenta of its supposed constituents. Consequently the angular momentum of a nucleus such as that of the nitrogen atom cannot be accounted for by the electron-proton concept. We would expect this particular nucleus to contain 14 protons and 7 electrons, or a total of 21 particles. Since protons and electrons have spin values of one-half integral each, the sum of the spins would be a half-integral. Actually the measured spin of the nitrogen nucleus is equal to 1, which agrees with the present postulated structure of 7 protons and 7 neutrons, or a total of 14 particles.

18 Fundamental Concepts of Inorganic Chemistry

1-7 The Proton-Neutron Concept. As early as 1920 scientists were dissatisfied with the electron-proton concept of nuclear structure. At that time W. D. Harkins, Ome Masson, and Sir Ernest Rutherford suggested, independently and almost simultaneously, that the nucleus might contain a neutral, uncharged particle, with a mass of unity on the atomic-weight scale. They believed such a particle resulted from the neutralization of the electric charge of the proton by the electron.

The discovery of the neutron by Chadwick in 1932 led to the rationalization of a new nuclear model to accommodate the neutral particle. In this new model the nuclei are composed of protons and neutrons. There must be enough protons to account for its charge, and the number of this charge is known as the *atomic number*. These protons will add up to a given mass; therefore sufficient neutrons must be present to account for the rest of the mass of the nucleus. The latter conclusion comes from the fact that the sum of the protons and neutrons is considered as giving approximately the mass of the nucleus. The helium nucleus (the alpha particle), for example, is believed to be an aggregation of two protons and two neutrons with an atomic mass of 4.

If the nucleus is assumed to contain only protons and neutrons, the question arises as to how other particles can escape from it. We have said that one strong argument in favor of the electron-proton concept was the emission of electrons in beta decay of radioactive elements. Accordingly some interpretation must be forthcoming to explain how these electrons are produced in a nucleus composed of neutrons and protons. In answer to this problem W. Heisenberg put forward the view that a neutron in the nucleus can sometimes be transformed into an electron and a proton, after which the electron escapes. The change in mass for such a beta decay is zero. The process of beta decay will be discussed more completely in a later chapter devoted to radioactivity.

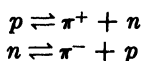
The numbers of protons and neutrons in the nuclei of the atoms of low atomic weights are nearly equal, but the relative number of neutrons becomes increasingly great for elements of higher atomic weights. The atomic weight of uranium, for example, is 238, and its atomic number is 92, indicating that the nucleus of the uranium atom is composed of 92 protons and 146 neutrons. On the other hand, the atomic weight of oxygen is 16, and its atomic number is 8; therefore the protons and neutrons in the nucleus must be equal in number.

1-8 The Meson Theory of Nuclear Forces. In the description of meson particles (Sec. 1-4) it was stated that these particles were predicted by Yukawa upon theoretical grounds in an attempt to explain the extremely strong forces which bind together protons and neutrons in the nucleus. Yukawa used the analogy between coulombic force and nuclear force as the basis for his prediction of meson particles.

Coulombic force represents an interaction of charged particles with a surrounding electromagnetic field; the energy of the field is quantized by photons. Hence, in the field theory, photons are assumed to form a field whose elements can be absorbed or emitted by electrons. In other words, electrons in an electromagnetic field may emit or absorb photons to or from the field. In this process photons transfer energy and momentum from one electron to another; thus they serve to transmit an electric force although they themselves have no electric charge.

In an analogous fashion to the absorption and emission of photons between electrons, neutrons and protons create a meson field, with the short-range nuclear forces arising as a result of the finite mass of the mesons. A neutron may be visualized as a proton surrounded by a statistical distribution of negatively charged pions, which are constantly emitted and reabsorbed. A proton may be similarly pictured as a neutron surrounded by a distribution of positively charged pions. As has been stated before (Sec. 1·4), Yukawa predicted that mesons should have a mass between 100 and 200 times that of an electron (this mass is today estimated as slightly less than 300 times) and should carry an electric charge.

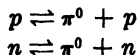
According to Yukawa, when a proton and neutron interact, the proton may emit a positive pion which is absorbed by the neutron; therefore, in the exchange of the positive pion, the proton becomes a neutron, and the neutron becomes a proton. In like manner a neutron may interact with a proton by emitting a negative pion, and in the process the neutron becomes a proton and the proton becomes a neutron. These two interactions may be represented as



The foregoing theory provides an explanation for the binding forces between protons and neutrons, or vice versa, between neutrons and protons, but it does not account for forces between like particles. If we assume that the nucleus is composed of two types of nucleons, neutrons and protons, which are held together by bonds produced by an interchange of particles, then it is also possible to assume that there are three types of binding particles. The positively and negatively charged pions take care of the neutron-proton bond, but there are two other types of bonds possible, namely, the neutron-neutron bond and the proton-proton bond. A proton cannot absorb a positive meson to acquire a second positive charge; consequently a charged meson cannot explain the proton-proton bond. Also, it is unlikely that a neutron can absorb a negative pion (a negatively charged particle of this mass has been postulated, but as yet it has not been discovered) in the formation of a neutron-

20 Fundamental Concepts of Inorganic Chemistry

neutron bond. To take care of the binding forces between like particles, N. Kemmer, the English physicist, reasoned that there must be a neutral meson. This neutral meson has since been discovered. The interactions between like particles may be indicated as



The neutral meson might also serve to carry forces between unlike particles as well as between like particles. In other words, according to Kemmer, the neutral meson could also explain the fact that nuclear forces are almost independent of the particles' charge (Sec. 1·5).

1·9 Magic Numbers, Nuclear Shell Structure. The considerable success attained in correlating chemical properties with orbital electron configuration (Sec. 4·1) has led to speculation as to the possibility of a similar concept for the arrangements of nucleons in the nucleus. It has been observed that atoms with an even number of nucleons in their nuclei are more plentiful in nature than those with an odd number. This would indicate that a nucleus made up of paired nucleons is more stable than one in which an odd nucleon is present. Additional facts may be correlated if it is assumed that the paired nucleons are also arranged in shells, after the fashion of planetary electrons.

It is recognized that neutral atoms containing a total of 2, 10, 18, 36, 54, or 86 extranuclear electrons are remarkably stable. The elements with atoms containing electrons of these totals are known as the *noble gases*, which are so inert that they form no chemical combinations. Atoms with one more or one less electron are unusually active chemically. This may be interpreted as a tendency on the part of the atom to achieve a stable, completed, outermost electronic shell. (For nuclei it so happens that those with 2, 8, 20, 50, 82, or 126 nucleons of the same kind are particularly stable. These numbers, which are sometimes referred to as "magic numbers," appear to be related to the completion of energy levels (shells) in the nuclei, just as certain numbers of electrons are required to fill the orbital levels of atoms. The evidence supporting a nuclear shell structure has been largely empirical in nature, although there has been some recent theoretical work to support this structure. Without going into details, some of the information which led to the idea of energy levels, or shells, in the nucleus was:

1. The binding energies of atomic masses in atoms with the magic-number nucleon totals, as calculated by the Einstein mass-energy equation (Sec. 1·10), are higher than their neighbors.

2. The abundance of stable atoms containing magic-number nucleon totals is greater than that of atoms with nucleon totals above and below these totals.

3. Nuclei with nucleon totals just above a magic number are less stable than those with magic-number totals. Such nuclei may be neutron emitters, and in the process of emitting neutrons they tend to attain the magic-number total. Nuclei of this type are extremely short-lived and occur only as intermediate products in processes involving artificial radioactivity (Sec. 8-10).

4. Radioactive atoms which are alpha emitters tend to attain the stable configuration associated with the magic-number totals.

In Chap. 2 a description is given of the building of electron orbits in the atom. In like manner one can picture the building of the structure of the nucleus as the gradual filling up of single-particle orbits by neutrons and protons. The orbits can be described by the same letters as those used to designate the quantized orbital angular momentum of electrons: $s = 0$, $p = 1$, $d = 2$, $f = 3$, $g = 4$, $h = 5$, $i = 6$. Since the neutrons and protons obey the Pauli exclusion principle (Sec. 2-24), the s level has room for just 2 protons and 2 neutrons, the p level has room for 6, etc. One of the proposed quantum configurations is given in Table 1-4. In this table the ordinary numbers refer to shells, the lower-case letters designate the orbitals, and the superscript numbers indicate the number of nucleons in each orbital.

TABLE 1-4 CLOSED-SHELL STRUCTURES IN THE NUCLEUS	
Shell	Configuration
2	$1s^2$
8	$1s^2 \quad 2p^6$
20	$1s^2 \quad 2p^6 \quad 2s^2 \quad 3d^{10}$
50	$1s^2 \quad 2p^6 \quad 3d^{10} \quad 4f^{14} \quad 5g^{18}$
82	$1s^2 \quad 2p^6 \quad 3d^{10} \quad 4f^{14} \quad 5g^{18} \quad 6h^{22} \quad 4d^{10}$
126	$1s^2 \quad 2p^6 \quad 3d^{10} \quad 4f^{14} \quad 5g^{18} \quad 6h^{22} \quad 7i^{26} \quad 5f^{14} \quad 3p^6 \quad 4p^6 \quad 2s^2$

1-10 Mass Defects in Atomic Nuclei. With the development of the mass spectrograph (Sec. 1-14) it is possible to determine atomic masses with a precision of approximately 1 part in 100,000. The mass of the proton has been determined as 1.00758, the mass of the neutron as 1.00893, and that of an electron as 0.0005486 mass unit. The scale used is the so-called *physical atomic-weight scale*, in which the mass of the O^{16} atom is taken as the standard and assigned a mass of exactly 16.00000 units. Since the numbers of protons, electrons, and neutrons in any atom are known (Sec. 1-7), and since the masses of the elementary constituents have been determined with a high degree of precision, it would be expected that the mass of an atom could be calculated accurately from these values. For example, the helium atom contains 2 electrons, 2 protons, and 2 neutrons; its mass should be

$$(2 \times 0.0005486) + (2 \times 1.00758) + (2 \times 1.00893) = 4.03411$$

22 Fundamental Concepts of Inorganic Chemistry

But actually the mass of the helium atom is 4.00390 units. The difference between the expected mass and the actual mass is

$$4.03411 - 4.00390 = 0.03021 \text{ mass unit}$$

and this difference is called the *mass defect*.

In the formation of the helium atom from its constituent particles a certain portion of matter, 0.03021 standard mass unit, to be exact, is converted into energy. (One standard mass unit equals 1.661×10^{-24} g.) This energy is in the form of binding force which holds the particles together, and most of it is concentrated in the nucleus as nuclear "glue" in binding together the two protons and two neutrons. The amount of energy created by the conversion of this amount of matter may be calculated from Einstein's mass-energy equation. This equation is stated as

$$E = mc^2$$

in which c is the velocity of light (3×10^{10} cm/sec.), m is mass, and E represents energy. Therefore the substitution of known values into this equation produces the following amount of energy:

$$E = 0.03021 \times 1.661 \times 10^{-24} \times (3 \times 10^{10})^2 = 4.5119 \times 10^{-5} \text{ erg}$$

Nuclear energy is customarily expressed in electron volts (ev) or million electron volts (Mev) rather than in ergs. The electron volt is defined as the energy necessary to raise one electron through a potential difference of 1 volt. Using the conversion factor between the two energy units, where $1 \text{ Mev} = 1.602 \times 10^{-6} \text{ erg}$, the binding energy for the helium atom may be expressed in million electron volts as

$$\frac{4.5119 \times 10^{-5}}{1.602 \times 10^{-6}} = 28.12 \text{ Mev}$$

Since the helium atom contains four particles, the binding energy per nucleon in He^4 is approximately 7.03 Mev. One standard mass unit equals 931 Mev.

1.11 Nuclear Binding Energies. The loss of mass, or mass defect, seems to be due almost entirely to the formation of the nucleus. In the preceding section we could just as well have omitted the masses of the electrons in the calculation of the mass defect for the helium atom. The packing together of the four nucleons in the confines of the helium nucleus not only results in their weighing less than when they are apart but also gives a measure of the binding forces operating within the nucleus.

A general equation for the calculation of the mass defect of any atom is

$$\text{Mass defect} = M_p Z + M_n (A - Z) - M$$

where M_p is the mass of the proton, Z is the atomic number (number of protons), M_n is the mass of the neutron, A is the mass number (total

particles in the nucleus), and M is the exact atomic mass. Since one standard mass unit, when converted into energy, gives rise to 931 Mev, the foregoing equation can be modified into a form suitable for the calculation of the binding energy of an atom, which is

$$\text{Binding energy, Mev} = 931[M_p Z + M_n(A - Z) - M]$$

Binding energy may therefore be defined as the energy released when a given number of protons and neutrons coalesce to form a nucleus, or, conversely, it is the energy required to disrupt a nucleus into its constituent protons and neutrons. The binding energies of typical nuclei are given in Table 1.5.

TABLE 1.5 BINDING ENERGIES OF TYPICAL NUCLEI

Element	Nucleus	Mass defect*	Binding energy, Mev	Binding energy per particle, Mev
Hydrogen . . .	$^1\text{H}^1$	0.00235	2.2	1.09
Helium . . .	$^2\text{He}^4$	0.0302	28.12	7.03
Lithium . . .	$^3\text{Li}^7$	0.0420	39.1	5.59
Beryllium . . .	$^4\text{Be}^9$	0.0623	58.0	6.44
Boron . . .	$^5\text{B}^{11}$	0.0814	75.8	6.89
Carbon . . .	$^6\text{C}^{12}$	0.0986	91.8	7.66
Nitrogen . . .	$^7\text{N}^{14}$	0.112	104	7.46
Oxygen . . .	$^8\text{O}^{16}$	0.137	127	7.94
Argon	$^{18}\text{Ar}^{40}$	0.368	342	8.57
Iron	$^{26}\text{Fe}^{56}$	0.523	487	8.70
Krypton	$^{36}\text{Kr}^{84}$	0.893	729	8.66
Tin.	$^{50}\text{Sn}^{118}$	1.080	1,011	8.52
Xenon	$^{54}\text{Xe}^{132}$	1.190	1,110	8.38
Lead	$^{82}\text{Pb}^{204}$	1.700	1,580	7.77
Uranium. . . .	$^{92}\text{U}^{238}$	1.900	1,780	7.45

* The unit is that of the physical atomic-weight scale; $^8\text{O}^{16} = 16.00000$.

Not too many conclusions can be drawn from Table 1.5 other than that the binding energies increase progressively with atomic mass and are fairly constant except for the very light elements. Far more information can be obtained by plotting mass number against binding energy per nucleon. Figure 1.1 is a plot of binding energy per particle against the mass number for stable nuclei and for a few of the heavy radioactive nuclei. From this plot the following observations are apparent:

1. There is a large central region with a mass-number range between 25 and 140, for which the binding energy per particle is nearly constant and equal to approximately 8.5 Mev/nucleon.

2. Nuclei with both small and large mass numbers have a smaller binding energy per particle; consequently these nuclei are less stable.

24 Fundamental Concepts of Inorganic Chemistry

3. Considerable irregularities occur for nuclei with small mass numbers.

In addition to the preceding observations concerning the plot shown in Fig. 1-1, certain qualitative inferences may be drawn which may, or may not, have some theoretical significance:

1. The value of 8.5 Mev/nucleon, which seems to be an average for a wide range of nuclei, may represent a saturation of binding energy forces. The idea that nuclear forces may have a saturation value was discussed in Sec. 1-5.

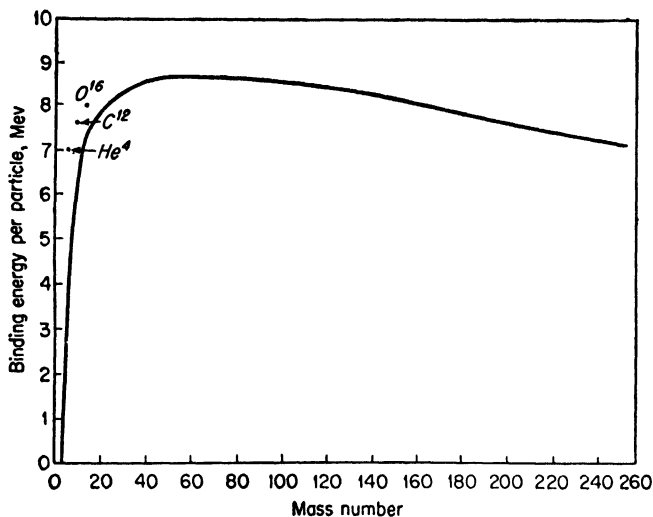


Fig. 1-1 Nuclear-binding-energy curve.

2. Beginning with the lighter nuclei, as the mass increases, the average binding energy per nucleon also increases because of a surface:volume ratio decrease. This effect may be compared with the surface tension of liquids.

3. The smaller binding energy per particle for nuclei with large masses results from coulombic repulsion of the large number of protons for each other in these nuclei. The coulombic forces produced by the large number of protons serve to neutralize the nuclear forces partially, especially as the radii of these nuclei increase; therefore nuclei with large masses are less stable than those with average masses.

The observations that have been made in regard to the binding-energy curve have some very important consequences. It is not unlikely that protons and neutrons are constantly forming helium atoms in the sun and that the sun's radiant energy is produced in this way. The so-called "hydrogen bomb" is the result of a series of nuclear transformations in

which relatively unstable nuclei, such as ${}^1_1\text{H}^3$, ${}^1_1\text{H}^2$, and ${}^3_3\text{Li}^6$, are converted into very stable ${}^2_2\text{He}^4$ nuclei. Possible nuclear reactions which produce stable nuclei from those which are less stable may be predicted from the binding-energy curve. Likewise, fission of the heaviest nuclei, such as those of uranium and plutonium, is energetically possible because the fission fragments are atoms whose nuclei have higher binding energies per nucleon.

Although Fig. 1-1 is important and useful in making practical observations and theoretical deductions, it does not give a complete picture of the variation in binding energy. The curve indicates average binding energies for certain stable nuclei, but the average may be quite different from the binding energy for each individual nucleon. Quite a different and more erratic curve is obtained if the binding energy for the last particle is plotted. What is even more desirable to know is the binding energy for every neutron and proton in all possible stable and unstable nuclei. However, a discussion of binding energies to that extent is beyond the scope of this book.

1-12 Nuclear Stability. The topic of nuclear stability is obviously so closely related to that of nuclear binding energies that this section may be conceived as being a continuation of the preceding one. Moreover the factors which enter into nuclear stability have been discussed or mentioned before. For the purpose of emphasis, and to tie some loose ends together, we shall summarize briefly the known facts relating to this topic.

In the analysis of nuclear stability we know that certain combinations of nucleons give rise to stable atoms, whereas others are unstable, undergoing radioactive decay. As yet it is impossible to predict exactly which combinations will be stable and which will be unstable; however, certain qualitative aspects of nuclear forces are sufficiently well understood to permit approximate predictions.

Stable nuclides with masses below 40 (atomic number 20) tend to have about equal numbers of neutrons and protons. Possibly the nucleons are entering particular energy levels, with one set of levels for protons and another for neutrons. Within this mass range no more than two protons and two neutrons with paired spins can enter in each energy level. In nuclides with masses above 40 the spacing for proton levels is apparently greater than the spacing for neutron levels, permitting the entrance of more neutrons than protons. Figure 1-2 is a plot for stable nuclides, showing the relation between mass number (total nucleons) and atomic number (number of protons). Since the number of neutrons in an atom is equal to the mass number minus the atomic number, it is apparent from this curve that the neutron:proton ratio increases with mass. Presumably this change in nucleon ratio results from increased coulombic

26 Fundamental Concepts of Inorganic Chemistry

repulsion of protons for each other. As the nucleus increases in mass (also size), the strong repulsive forces acting between increased numbers of protons (coulombic forces vary as the square of the reciprocal of the distance of separation) require more neutrons to bind them together. Figure 1.3 is a plot showing the increase of the neutron:proton ratio with

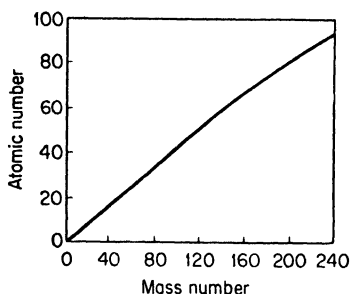


Fig. 1.2 A plot for stable nuclides, showing the relation between mass number and atomic number.

atomic number (number of protons). However, the coulombic force of repulsion is negligible in nuclides of small mass. This results

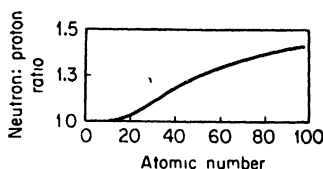


Fig. 1.3 Change of neutron:proton ratio with atomic number.

from the much greater strength of nuclear force as compared with coulombic force between two particles. As we have said before, the coulombic force operating between two protons separated by a nuclear distance is approximately 40 times less than the nuclear force binding together the same two particles.

Nuclear forces are frequently called “exchange forces” because the

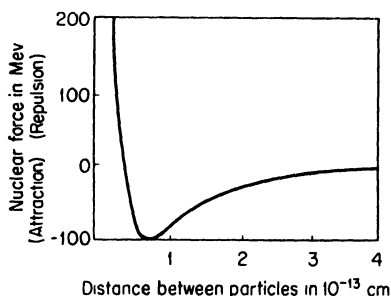


Fig. 1.4 The variation of nuclear force with distance between particles.

forces between nucleons (protons and neutrons) result from an exchange of matter or energy (or both) in the form of quanta of energy or units of matter, the latter being collectively known as *mesons*. Nuclear force is immense as compared with other forces. The average binding energy per particle, as indicated on the binding-energy curve in Fig. 1.1, is approximately 8.5 million ev for a large number of stable nuclei, whose masses are

neither very small nor very large. Nuclear forces operate only over very short distances and vary greatly with change in distance. The force of attraction (binding energy) apparently reaches a maximum at a distance of about 8×10^{-14} cm. At distances less than this value the force of attraction decreases rapidly and, at approximately 5×10^{-14}

cm, changes into a force of repulsion. At distances greater than that corresponding to maximum attraction, nuclear forces between particles decrease somewhat less rapidly and approach zero in the neighborhood of 4×10^{-13} cm. The variation of nuclear force with distance between particles is indicated in Fig. 1-4.

The decrease in nuclear forces with increased distance between particles accounts to some extent for the instability of nuclides of large masses. This instability is accentuated because of the sizable coulombic forces resulting from the presence of a large number of protons, since coulombic forces act in opposition to nuclear forces.

The relatively smaller binding energies (nuclear forces) operating in nuclides of small masses (Fig. 1-1) can be interpreted as partly due to a nuclear surface-tension effect. Particles at the surface of a nucleus cannot interact with as many of their neighbors as can those in the interior. This effect increases with high surface:volume ratios, which increases with a decrease in mass. In other words, the particles at the surface of the nucleus will not be bound so tightly as those in the interior; consequently the binding energy of the nucleus as a whole is decreased by an amount which varies with its surface area.

ISOTOPES

It is practically impossible to explain any principle or discuss any broad topic in chemistry without referring to some other unexplained principle or undiscussed topic. So it was in the discussion of nuclear structure. Although at no time was the word *isotope* used in the explanation of nuclear structure, actually the underlying idea conveyed by the term was used a number of times. Furthermore we shall have occasion to use this word or the idea it implies throughout our book. Even more important, the topic of isotopes is an essential subtopic for discussion in the present chapter devoted to a study of atomic nuclei. For these many good reasons we shall define this term forthwith. *Atoms of a given element which differ in atomic mass but which have the same nuclear charge (atomic number) are called isotopes.* Since the different varieties of atoms of the same element have the same atomic number, their atoms contain the same number of electrons and protons, and, in consequence, have almost identical chemical and physical properties. Atomic number has been defined as the number of planetary electrons that an atom possesses, or it may also be defined as the number of positive charges (protons) contained in the nucleus. Since the two particles are equivalent in number within a neutral atom, either definition will suffice. The difference in atomic mass among isotopes of the same element is due to the same number of protons being combined with *unequal* numbers of

28 Fundamental Concepts of Inorganic Chemistry

neutrons. For example, a ${}_{17}\text{Cl}^{35}$ nucleus contains 17 protons and 18 neutrons, whereas a ${}_{17}\text{Cl}^{37}$ nucleus contains 17 protons and 20 neutrons. The relative masses of individual atoms are very close to—but not quite (Sec. 1·10)—whole numbers when expressed on the physical atomic-weight scale. The values observed in the mass spectrograph for the natural isotopes of chlorine are 34.97867 and 36.97750. The nearest integers, 35 and 37, are the respective mass numbers. The fractional atomic weight of chlorine, 35.457, results from the fact that the element occurs in nature as a mixture of constant composition, containing 75.4 per cent of the lighter and 24.6 per cent of the heavier isotope.

With this brief introduction on the subject of isotopes we shall enter into a more comprehensive treatment of the topic.

1·13 Historical. In 1803 John Dalton laid the foundations of modern chemistry in the postulates of his atomic theory. Of these several postulates only one is partly invalid today, and that is the one in which he states: "Atoms of the same element are similar to one another and equal in weight." We now know that he was in error in respect to the latter part of this statement. Equality of weight is not a characteristic of all atoms of the same element. Some 10 years later William Prout suggested that the atoms of the elements were all made up of aggregations of the same primordial atoms, which he called "protyle." Furthermore he said that the combining weights of *all* the elements should be whole numbers. Thus we see that, over a century and half ago, chemists were faced with a choice of two theories as to the constitution of the atom. Accumulative evidence from accurate atomic-weight determinations indicated that many elements were composed of atoms with fractional weights, and, regardless of the fact that the idea of atoms with fractional weights appears totally illogical to us at the present time, this evidence caused the Prout theory to be abandoned. The postulate that atoms of the same element are identical in weight could not be challenged by chemical methods, and in the early part of the nineteenth century chemists chose to follow the sound working hypothesis of John Dalton rather than the philosophical speculation of William Prout. Just how many years this unfortunate choice of theories delayed the advancement of theoretical chemistry cannot be safely estimated. Certainly there is no record of Dalton's postulate regarding atomic weights being challenged until during the 1880s.

Paul Schutzenberger was probably the first scientist after Prout to question the Dalton concept of atomic weights. Between 1880 and his death in 1897 he became convinced that the elements were all formed by the same process of condensation from one primordial substance of very small atomic weight. He also held that the atomic weight of a given element could vary within narrow limits and be modified according

to the conditions under which a compound was found. A much clearer idea as to the variation of weights among atoms of the same element was expressed in 1886 by Sir William Crookes in his presidential address to the Chemical Section of the British Association at Birmingham. In this address he said:

I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on.

Sir William's ideas in regard to the variability of atomic weights for atoms of the same element were influenced by the similarity of the rare earth elements. During this period he separated the earth yttria into a number of components which had different phosphorescent spectra but resembled each other very closely in their chemical properties. He called these components "meta elements" and endeavored to prove that they were atoms of the same element but with differing atomic weights. Unfortunately the prophetic insight displayed in his Birmingham address was not carried into his research with the rare earth elements. Subsequent investigations by others proved that the meta elements were actually different elements. Sir William's failure in the rare earth field reinforced scientific faith in the original Dalton postulate. It was not challenged again for over two decades.

To Frederick Soddy,¹ an English physicist, goes the credit of first recognizing and interpreting correctly the idea of the existence of isotopic masses. The existence of such masses was first realized in the study of radioactive elements. This might have been expected since radioactive change is associated with disintegration of the nucleus. After studying the occurrence of chemical identities among the products of radioactivity, Soddy, in 1910, stated: "Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several of different atomic weights, or that any atomic weight is not merely a mean number."

Soddy was also one of the first to recognize the law associated with the decay of radioactive elements, which in terms of present-day chemistry may be stated to the effect that the emission of an alpha particle from the nucleus of a radioactive element corresponds with a reduction of the atomic number by two units and a diminution of the atomic weight by four units, while the emission of an electron increases the atomic number by one unit but leaves the atomic weight unchanged. This rule explains the existence of radioactive isotopes. In accounting for chemical identities with different atomic weights, among the radioactive elements, Soddy used the following words:

¹ F. Soddy, *Ann. Repts.*, 7: 286 (1910).

30 Fundamental Concepts of Inorganic Chemistry

The same algebraic sum of the positive and negative charges in the nucleus when the arithmetical sum is different gives what I call "isotopes" or "isotopic elements" because they occupy the same place in the periodic table. They are chemically identical, and save only as regards the relatively few physical properties which depend upon atomic mass directly, physically identical also.

Although the occurrence of isotopes was first recognized among radioactive elements by Soddy and his coworkers, it remained for Sir J. J. Thomson and F. W. Aston, in the decade which followed, to prove that most of the ordinary elements are mixtures of isotopes.

1.14 The Detection and Study of Isotopes. In discussing the discovery of the proton (Sec. 1.3) we learned that, if a perforated cathode is used in a cathode-ray tube, luminous rays emerge in straight lines from

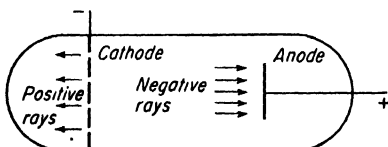


Fig. 1.5 Positive-ray tube.

the holes in the cathode and move in a direction opposite to the cathode rays. These luminous rays are deflected in either an electric or a magnetic field, and in the direction opposite to the deflection of electrons in the same fields, indicating

that they are streams of positively charged particles. Originally called "canal rays," the more appropriate name of *positive rays* was proposed for them in 1907 by J. J. Thomson. Figure 1.5 is a sketch of a positive-ray tube. A determination of the ratio of charge:mass of the particles making up the positive rays indicated that the lightest of these had a mass approximately that of the hydrogen atom. This light particle was eventually designated the *proton*.

During the course of investigating positive rays over a number of years Sir J. J. Thomson had by 1912 constructed in the Cavendish Laboratory of Cambridge University a much improved version of the original positive-ray apparatus. In Fig. 1.6 the improved apparatus is represented schematically. An electric discharge is passed through the discharge tube containing the experimental gas at low pressure, causing the production of positive ions. A few of the ions, accelerated by attraction to the cathode, pass through a small opening in the cathode into a space which is subjected to the action of parallel magnetic and electric fields. The electric field is applied to soft iron plates P , P' which are placed between the poles M , M' of a powerful electromagnet. P and P' also constitute the pole pieces of the magnet but are electrically insulated from it by strips of mica. After passing through the electric and magnetic fields, so arranged as to give deflections at right angles to one another, the positive ions impinge upon a photographic plate H . The results obtained by this method are indicated upon the developed plate

in the form of a series of parabolic streaks, each corresponding to a definite value of the mass:charge ratio for atomic and molecular particles present in the positive rays. Absolute masses are determined by calibrating the instrument against a substance of known mass, such as oxygen.

The results of the Thomson "parabola" method are not easy to interpret. Any ionizable material in the discharge tube will give a parabola; consequently the sample must be of the highest purity. Another problem is the gaining of electrons by ions, through collisions, while passing

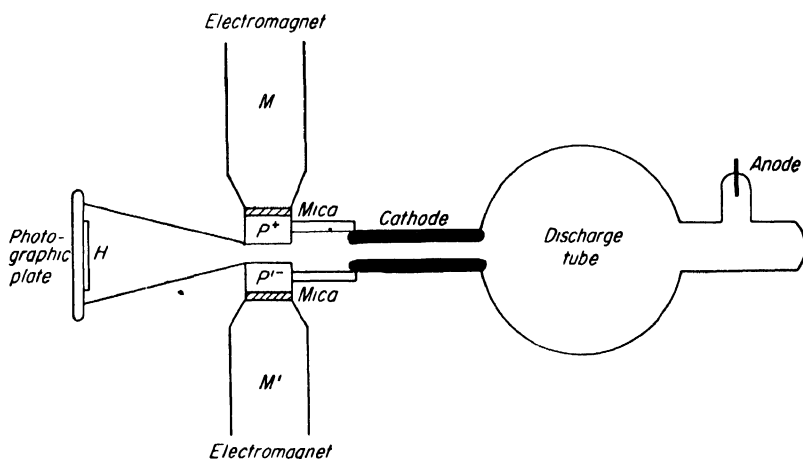


Fig. 1-6 Thomson's positive-ray apparatus (parabola method).

through the deflecting fields. The resulting atoms or molecules, which Thomson called "secondary rays," appear on the plate either as a fog to obscure the desired results or as additional parabolas to confuse the interpretation of those parabolas produced by charged particles. The parabola method also suffers from an inherent fault through its lack of resolving power, which leads to deceptive photographic effects. F. W. Aston has stated that this method is fundamentally unsuited to critical investigations of any but the lightest elements.

During the investigation of the constituents of the air by the parabola method Thomson, in 1912, obtained on the photographic plate two lines for neon corresponding to masses of 20 and 22. At the time of this discovery he gave the wrong interpretation for the two parabolas. In discussing the two lines, he said: "There can be little doubt that what has been called neon is not a single gas, but a mixture of gases, one of which has an atomic weight of about 20 and the other about 22. The parabola

32 Fundamental Concepts of Inorganic Chemistry

due to the heavier gas forms only a small percentage of the mixture." However, subsequent experiments with purer samples of neon indicated that the two lines must be due to isotopes of neon. This was the first evidence of the existence of isotopes among the stable elements.

The *mass spectrograph* is an instrument designed for determining the relative masses of atoms and molecules. The operation of this apparatus is based on the deflection of electrically charged ions or molecular fragments in either an electric or a magnetic field, or both. The magnitude of deflection for an ion is a function of the ratio of the charge of the ion to its mass. Our knowledge of the existence of isotopes among the stable

elements has been derived from evidence provided by these instruments. Following Thomson's success in showing that neon was composed of two isotopes with his parabola method of positive ray analysis, a number of mass spectrographs were built for the purpose of isotopic analysis. The early instruments were designed for determining the relative abundance of stable isotopes; later ones were for the precise determination of mass. It is beyond the scope of this book to discuss many of these instruments, excellent though they

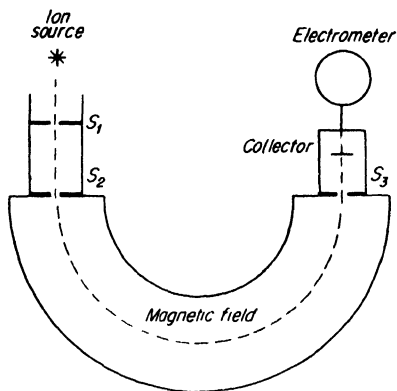


Fig. 1-7 Sketch of Dempster's mass spectrograph.

may be, or even to list the various investigations in the field of isotopic analysis and mass determinations. Except for Thomson's apparatus, which has already been described, we shall confine our descriptions of mass spectrographs to those of Dempster and Aston. Our choice is based on the fact that they were the earliest instruments to be designed and, for that reason, of greater interest historically.

Early designers of mass spectrographs were faced with the problem of devising an apparatus which would focus a beam of ions containing species with widely different velocities. One of the first instruments, if not the first, to overcome this difficulty was designed and built by A. J. Dempster, between 1918 and 1922, at the Ryerson Physical Laboratory of the University of Chicago. The method he used was essentially the one employed by Classen, in 1907, for the determination of e/m for electrons. In this method a narrow ray of positive ions is isolated by slits and bent into a semicircle by a strong magnetic field. The ray then passes through a final slit and falls on a plate connected to an electrometer. The potential difference through which the particles fall, the strength of the mag-

netic field, and the radius of the curvature of the field determine the ratio of the charge to the mass of a particle within the ray. A sketch of the Dempster apparatus is shown in Fig. 1-7.

The Dempster method is more suited to the study of less volatile substances than the one used by Thomson. In this method the element under study is vaporized by heating it electrically and the metallic vapor then subjected to bombardment by electrons from a hot filament. Some of the positive ions produced by this bombardment pass through the slit S_1 indicated in the diagram. Between S_1 and S_2 they are accelerated by an electric field which gives them all approximately the same kinetic energy, which is thousands of times greater than their average thermal energy. Since they now all have practically the same kinetic energy, the lighter ones must have less momenta than the heavy ones. Upon entering the magnetic field at slit S_2 the ions move perpendicular to the field and in semicircular paths of radii proportional to their momenta. Therefore the light ions will move in smaller semicircles than the heavy ones. Only those particles of suitable mass are able to pass through the slit at S_3 , to be collected on an insulated plate and their number measured as a current on an electrometer. The magnetic field must be adjusted to the proper value, and this value varies for each isotope, to permit the proper bending and focusing so that an ion of a given isotope may pass through the slit system. By plotting the electrometer current against the magnetic field the various isotopes appear as peaks of current; consequently the abundance of the isotopes may be compared by comparing the heights of their individual peaks. Magnesium was the first metal to be analyzed by means of this method. In 1920, Dempster¹ announced the discovery of three isotopes for magnesium, with mass numbers 24, 25, and 26. The curve he obtained for magnesium is typical for the method and is shown in Fig. 1-8.

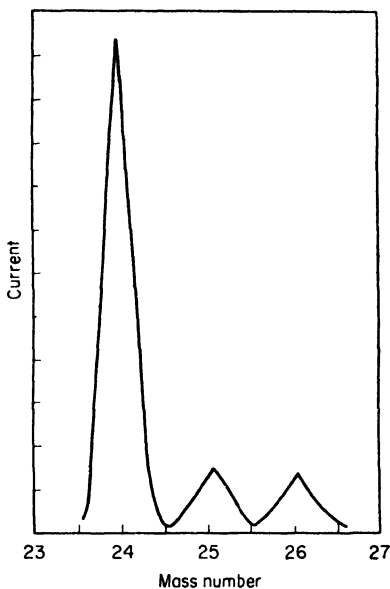


Fig. 1-8 Curve obtained for magnesium with Dempster's mass spectrograph.

F. W. Aston was an assistant to J. J. Thomson during the time of the

¹ A. J. Dempster, *Science*, **52**: 559 (1920).

34 Fundamental Concepts of Inorganic Chemistry

latter's pioneer work with the parabola method for positive-ray analysis. In fact it was Aston who partly separated neon into two fractions of different atomic weights by repeated diffusion. These two fractions, when subjected to positive-ray analysis, give convincing proof of the existence of two isotopes for neon.

Aston redesigned Thomson's positive-ray-deflection apparatus and in 1919 constructed an instrument with ten times the resolving power of Thomson's parabola method. This instrument, which gained him the credit of being the inventor of the mass spectrograph and the Nobel prize in 1922, was so designed that all particles having the same mass were brought to a focus, by the electric and magnetic fields, to produce a fine

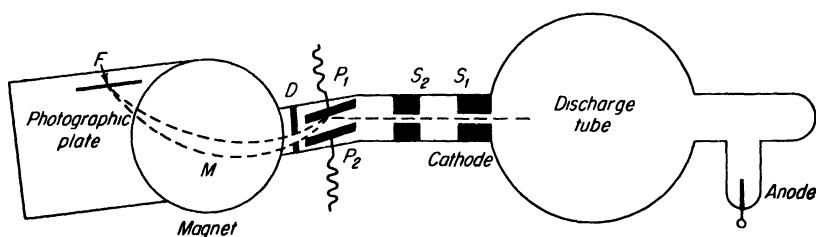


Fig. 1-9 Diagram of Aston's first mass spectrograph.

line upon the photographic plate rather than a parabola. Therefore, in this method, the photographic plate actually becomes a mass spectrum, since each line upon it indicates the presence of atoms or molecules of a particular mass.

The principle of Aston's first spectrograph is shown in Fig. 1-9. As in the Thomson instrument a narrow beam of positive rays passes from a cathode tube through a narrow opening in the cathode. The rays are sorted into a thin ribbon by means of two parallel slits S_1 and S_2 and then spread out into an electric spectrum by the action of the parallel charged plates P_1 and P_2 . The spreading of the heterogeneous ribbon of rays, formed by the slits, results from a difference in velocity among the particles making up the rays. The slower rays are deflected downward more than the faster ones. A portion of this spectrum is deflected at an angle determined by the slope of plates P_1 and P_2 . The resulting narrow pencil of rays, further selected by diaphragm D , passes through a powerful magnetic field at right angles to the electric field and to the plane of the paper. (A section of the circular electromagnet which is in the plane of the paper is represented in the sketch by the circle M .) Here again the faster particles are deflected more than the slower ones, but the action of the magnetic field is to bend the rays back again (upward) through an angle that is more than twice that produced by the electric field. This results in all particles (rays) with the same value of

charge:mass ratio e/m being focused at F in the form of a single straight line perpendicular to the plane of the paper. If a photographic plate is placed at the point of focus, as indicated in the sketch, particles with different e/m values produce a series of lines on the plate. The developed plate is called a mass spectrum since the positions of the lines depend upon mass and the intensities upon number of particles.

Although convincing evidence of the existence of two isotopes for neon has been demonstrated by means of Thomson's parabola method for positive-ray analysis, final proof of these isotopes was published, in 1919, by Aston¹ immediately following the completion of his mass spectrograph. A few weeks later the isotopic composition of chlorine and mercury was demonstrated, and during the succeeding months progress in isotopic analysis of the elements was most rapid. By the end of 1920 Aston had analyzed 19 elements in his mass spectrograph and found that 9 of them existed in two or more isotopic forms. Other mass spectrographs were built, and other physicists joined in the search for isotopes of the various elements. By 1935 only platinum, palladium, gold, and iridium had not been analyzed successfully. The passive chemical properties of these elements had contributed to the defeat of all attempts to obtain their mass spectra. It was not until 1935 that Dempster, by his vacuum-spark method, was able to obtain mass spectra for these 4 elements. Since that time a number of rarer isotopes have been found, and it is quite likely that others will be, also, but with regard to the identification of the principal isotopes of the various elements the investigation may be considered as having been completed.

1-15 The Whole-number Rule and Packing Fraction. By the end of 1920 Aston had examined 19 elements in his mass spectrograph. For a variety of reasons he based the masses of the isotopes so discovered upon the scale $O = 16$. (This was before the discovery that oxygen existed as three isotopes.) One of the first generalizations emerging from the relative mass determinations of isotopes was the fact that these masses were very close to whole numbers. The results he obtained led Aston, in early 1920, to formulate the *whole-number rule*, which was essentially a remodeled version of the Prout hypothesis. According to this rule the masses of the atoms are nearly integers on a scale such that oxygen equals 16. Furthermore, the fractional atomic weights of the elements are due to the presence of two or more isotopes, each of which has an atomic mass that is approximately a whole number.

Aston's first mass spectrograph was not sufficiently accurate to substantiate by experiment the theory of his whole-number rule. Accordingly he bent his efforts toward building an instrument which would be able to determine the divergences, if any, of isotopic masses from the

¹ F. W. Aston, *Phil. Mag.*, **39**: 449 (1920).

36 Fundamental Concepts of Inorganic Chemistry

whole-number rule. The improved second mass spectrograph was completed in 1925 and used with slight modifications during the following 10 years. This apparatus had five times the resolving power of the first one and was capable of giving results that were accurate to about 1 part in 10,000. The new instrument was immediately put to work in redetermining the masses of well-known isotopes and to ascertain the divergences of the masses of these atoms from whole numbers. As with the first mass spectrograph the isotopic masses were based upon the mass of oxygen as

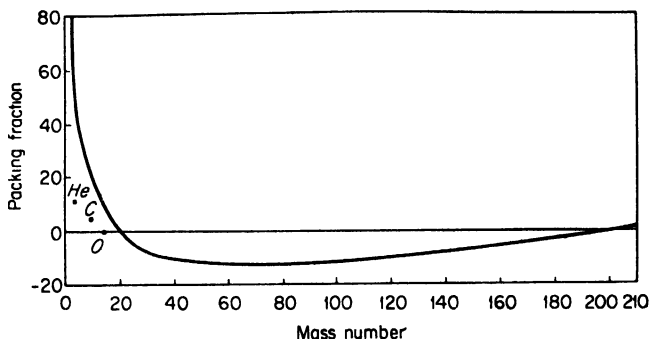


Fig. 1 10 Aston's original packing-fraction curve (1927).

16, since it was not until about 1929 that the proof of the existence of isotopes of oxygen was published.

By 1927 Aston had examined about 20 elements in his second mass spectrograph and was able to show that the masses of isotopes of these elements actually differed slightly from whole numbers. Aston called the difference between the isotopic mass and the nearest whole number, divided by the isotopic mass, the packing fraction. It represents the average gain or loss in mass per unit of mass in the atom under examination, as compared with the state of nuclear packing in oxygen.

The numerical values of the packing fractions were so small that Aston multiplied these values by 10,000 in order to secure figures which were easier to record and to indicate by graphic means. Upon plotting the packing fractions for the stable isotopes of the various elements against their mass numbers Aston found that these values, with the exception of He^4 , C^{12} , and O^{16} , fell upon a smooth curve (Fig. 1-10). This curve falls from hydrogen, with a packing fraction of +78, to zero at a mass between 16 and 20, and then, after passing through a flat minimum of about -10 in the neighborhood of mass 50, it rises almost linearly to recross the zero axis at a mass number of about 200.

The implications of the packing-fraction curve are the same as those indicated in the nuclear binding-energy curve which was sketched in

Fig. 1-1. In fact each curve is simply an inverted form of the other. However, the nuclear binding-energy curve is more precise and, consequently, of more theoretical importance. Yet even as early as 1927 the packing-fraction curve indicated the relative nuclear stabilities. From this curve it is evident that the lighter nuclei, with the exception of He^4 , C^{12} , and O^{16} , are less stable than those of intermediate mass. Also, of apparent significance is the fact that the minimum in the packing-fraction curve is near the atomic masses of the atoms of iron and nickel. These atoms, representing a maximum of nuclear stability, are believed to be concentrated largely in the core of the earth. The nuclei with mass numbers above that of mercury have positive packing fractions, indicating increasing instability. This agrees with the experimental observations of the radioactive decay of those elements with heavy nuclear masses.

1-16 Chemical and Physical Atomic-weight Scales. For many years oxygen has been the primary standard for chemical atomic weights. The selection of this standard resulted from oxygen's relative abundance in nature and its chemical activity with other elements. As a consequence of its wide occurrence, not only in the atmosphere but also in chemical combination, it is not surprising that oxygen should have appeared to some extent in all the discharge tubes used in the early work on positive-ray analysis. Therefore its molecular line at 32, and its atomic lines of the first and second order at 16 and 8, were chosen as convenient standards of mass. Up to 1929 no isotopes had been discovered for oxygen, and since it was believed to be composed entirely of O^{16} atoms, the mass of this atom was arbitrarily assigned a mass of 16.00000.

In 1929 F. W. GIAUQUE and H. L. JOHNSTON¹ published results showing that atmospheric oxygen is not a single species of atom, as formerly believed, but is composed of three isotopes, with mass numbers 16, 17, and 18. This discovery necessitated a revision of mass determinations and led to a new primary standard for mass spectrographic values. The new scale, or standard, which is called the *physical atomic-weight scale*, uses the mass of an atom of O^{16} as the primary standard and has assigned to this atom, arbitrarily, a mass of exactly 16.00000 units. The O^{16} atom is the most abundant isotope of oxygen, comprising 99.757 per cent of this element, and the difference between the *physical atomic-weight scale* and the *chemical atomic-weight scale* is not great.

Before the discovery of the isotopes of oxygen the chemical atomic-weight scale was based, as was the physical, on the atomic weight of the O^{16} atom and assumed that the element oxygen contained only this atom. Since the discovery of the three isotopes for oxygen, no change has been made in this scale, but we now define it somewhat differently. The

¹ F. W. GIAUQUE and H. L. JOHNSTON, *Nature*, **123**: 318 (1929).

38 Fundamental Concepts of Inorganic Chemistry

chemical atomic-weight scale is based on the atomic weight of the natural isotopic mixture of the O^{16} , O^{17} , and O^{18} atoms. It is actually the average weight of the mixture, to which has been assigned the value of exactly 16.00000. The unit in the chemical scale is larger than the one used in the physical scale, because the standard of 16.00000 is equivalent to a weighted average of the three isotopic masses. On the other hand, physical atomic weights are always larger than the chemical values, because the physical scale is based on 16.00000, which is slightly less than the weighted mean of the three isotopes. The conversion factor between the two scales is 1.000275, as used by the Committee on Atomic Weights of the American Chemical Society in 1951. The difference between the two scales for atomic weights can be shown more clearly by indicating how the factor is obtained.

On the physical scale the exact masses of the three isotopes of oxygen are: $O^{16} = 16.00000$ (this is the standard), $O^{17} = 17.00450$, and $O^{18} = 18.0019$. The percentages in which these isotopes occur in normal oxygen are 99.76, 0.04, and 0.20 for the O^{16} , O^{17} , O^{18} atoms, respectively. The weighted mean of these values is 16.0044 on the physical scale and is obtained as follows:

$$16.00000 \times 0.9976 = 15.9616$$

$$17.00450 \times 0.0004 = 0.0068$$

$$18.0049 \times 0.0020 = 0.0360$$

$$\text{Weighted mean} = 16.0044$$

The weighted mean, 16.0044, is used on the chemical scale as equal to 16.00000; therefore the physical atomic weight is always larger than the chemical value by the factor obtained by dividing 16.00000 into 16.0044, or

$$\frac{16.0044}{16.00000} = 1.000275$$

To illustrate the conversion factor with a specific example, suppose the chemical atomic weight of phosphorus is 30.975, and it exists only as one isotope, P^{31} ; what is the physical atomic weight of the P^{31} atom?

$$30.975 \times 1.000275 = 30.984$$

On the other hand, if the physical atomic weight of the F^{19} atom is 19.00450, what is the chemical atomic weight of this atom?

$$\frac{19.00450}{1.000275} = 18.9993$$

The chemical method of accurately determining atomic weights involves the determination of stoichiometric ratios, based on the scale

O = 16.00000. However, the stoichiometric ratios must necessarily involve elements other than oxygen; e.g., the atomic weights of many elements have been determined by the halide ratios *metallic halide:silver* and *metallic halide:silver halide*. The calculation of atomic weights from these halide ratios presupposes a knowledge of the atomic weight of silver and the halides, usually chlorine or bromine, on the oxygen scale. A number of different methods have been developed for the determination of chemical atomic weights, but the one that has been most frequently used is based on the accurate determination of the equivalent weight of an element. A typical example of this method is the determination of the atomic weight of potassium by G. P. Baxter and W. M. MacNevin.¹ In this determination potassium perchlorate, purified by a number of crystallizations, was converted into the chloride by heating in a platinum dish. The chloride was further purified by two precipitations with hydrogen chloride. The potassium chloride thus obtained was dissolved in pure water and diluted until approximately 0.05 N. A nearly equivalent quantity of pure silver was weighed and, after solution in nitric acid, was diluted to a similar concentration. The resulting silver nitrate solution was slowly added to the potassium chloride solution and the precipitate of silver chloride allowed to stand until equilibrium had been attained. The slight excess of silver ions was determined by means of a nephelometer. The atomic weight of potassium was found by the ratio

$$\frac{\text{K} + 35.457}{107.880} = \frac{\text{weight of KCl}}{\text{weight of Ag}}$$

After all weights had been corrected to a vacuum basis, the average atomic weight of potassium was computed to be 39.094.

The foregoing method for determining atomic weights was first used by J. J. Berzelius, who within a little more than 10 years, between 1807 and 1818, determined the combining weight of 43 elements. The method was later improved by Stas, whose precise determinations of atomic weights caused the Prout hypothesis to be discarded. Since the turn of the century, more than half the present accepted chemical atomic weights, determined by various methods, have been made under the supervision of three men, T. W. Richards and G. P. Baxter of Harvard, and O. Honigsmid of Munich. The Nobel prize was awarded to T. W. Richards in 1914 for his work along this line.

The high degree of accuracy which may be attained with improved mass spectrographs and the fact that chemical atomic weights may be calculated from isotope-abundance data have enabled a comparison to be made between the two methods, physical and chemical, for determining mass. In quite a number of instances the values have not agreed with

¹ G. P. Baxter and W. M. MacNevin, *J. Am. Chem. Soc.*, **55**: 3185 (1933).

40 Fundamental Concepts of Inorganic Chemistry

each other, and invariably a redetermination of the chemical atomic weight has indicated the superior accuracy of the mass spectrograph over chemical methods. The values which are obtained by the physical method are precise to better than 1 part in 10,000, which is a precision rarely met with in chemical analysis. It is interesting to note that the Commission of Atomic Weights of the International Union of Pure and Applied Chemistry in its meeting in New York in September, 1951, adopted changes in the chemical atomic weights of seven elements,¹ aluminum, silicon, phosphorus, potassium, scandium, krypton, and iodine. All seven changes were the result of more accurate determinations by mass spectrographic methods.

To illustrate the influence of the mass spectrograph on the evaluation of chemical atomic weights, consider the recent change in the atomic weight of silicon. Originally the atomic weight had been set at 28.05, based largely on the work of Baxter, Weatherill, and Scripture.² In 1951 K. T. Bainbridge and A. O. Nier³ indicated the best values for the isotopic abundance of Si^{28} , Si^{29} , and Si^{30} to be 92.27, 4.68, and 3.05 per cent, respectively. During the preceding year H. E. Duckworth and coworkers⁴ had determined the masses of the three isotopes (on the physical scale) as 27.9858, 28.9858, and 29.9831, respectively. With the foregoing data and the conversion factor of 1.000275 between the physical and chemical scale the new value for the atomic weight of silicon was calculated as follows:

$$\begin{aligned} 27.9858 \times 0.9227 &= 25.8225 \\ 28.9858 \times 0.0468 &= 1.3565 \\ 29.9831 \times 0.0305 &= 0.9145 \\ \text{Weighted mean} &= 28.0935 \end{aligned}$$

The weighted mean is the chemical atomic weight; accordingly the value 28.09 was the revised figure chosen for the 1951 table of atomic weights by the Committee on Atomic Weights.

The advantages of the physical atomic-weight scale are readily apparent. The reader may wonder why this scale has not also been adopted by chemists as well. In part answer to this question we quote from the Report of the Committee on Atomic Weights of the American Chemical Society in 1951:⁵

¹ *J. Am. Chem. Soc.*, **74**: 2447 (1952).

² G. P. Baxter, P. F. Weatherill, and E. W. Scripture, *Proc. Am. Acad. Arts Sci.*, **58**: 246 (1923).

³ K. T. Bainbridge and A. O. Nier, Relative Isotopic Abundance of the Elements, *Nat. Research Council U.S. Preliminary Rept.* 9 (1951), Nuclear Science Series.

⁴ H. E. Duckworth and coworkers, *Phys. Rev.*, **79**: 188, 402 (1950).

⁵ *J. Am. Chem. Soc.*, **74**: 24,447 (1952).

From time to time proposals are made to change the basis of the chemical scale to 16 and thus end the difference between the chemical and physical scales. The atomic weight of natural oxygen, with which the chemist is usually concerned, would then become 16.0044, and all the other values of the present table would be similarly multiplied by the factor 1.000275. This would affect nearly all relatively recently published values of atomic and molecular weights, as well as a great mass of data on the properties of systems recorded on a molar or "equivalent" basis. It is believed that the confusion that would result would be too high a price to pay for the advantage gained. Relatively few scientists are concerned with both the chemical and physical scales.

There is little doubt that the superior accuracy of improved mass spectrographs will result in many other changes in the present accepted chemical atomic weights. The irony of these changes makes pertinent a quotation from a published lecture given by F. W. Aston,¹ in 1938, at Cambridge University. In this lecture Aston quotes from a statement attributed to Frederick Soddy, in 1932, regarding the determinations of atomic weights:

After many vicissitudes and the most convincing apparent disproofs, the hypothesis thrown out so lightly by Prout, an Edinburgh physician, in 1805, has, a century later, become the corner-stone of modern theories of the structure of atoms. There is something surely akin to if not transcending tragedy in the fate that has overtaken the life work of that distinguished galaxy of nineteenth century chemists, rightly revered by their contemporaries as representing the crown and perfection of accurate scientific measurement. Their hard won results, for the moment at least, appear as of as little interest and significance as the determination of the average weight of a collection of bottles, some of them full and some of them more or less empty.

1-17 Abundance of Isotopes. The elements exist in nature with certain relative isotopic abundance. For most of the elements the relative abundances of their isotopes have been found to be independent of the sources of the material. This is not always true; one of the best-known exceptions is the differences in abundance ratios exhibited by lead samples secured from a variety of sources. For example, lead extracted from uranium minerals contains more of the 206 isotope, whereas that found in thorium minerals has more of the 208 isotope. In fact these differences in abundance ratios for lead enabled Frederick Soddy, in 1910, to predict the existence of isotopes. It should be pointed out that the wide differences in abundance ratios for lead occur in this element only when it is an end product of radioactive decay. Lead samples obtained from apparently nonradioactive sources exhibit only slight differences in isotopic

¹ F. W. Aston, *Forty Years of Atomic Theory*, "Background to Modern Science," Cambridge University Press, New York, 1938.

42 Fundamental Concepts of Inorganic Chemistry

composition, and these differences are never pronounced. Slight differences have also been found in a few other elements. Sr^{87} is present in abnormal amounts in rubidium-containing minerals. The $\text{C}^{12}/\text{C}^{13}$ ratio varies somewhat with source; in coal it is 91.8, whereas in limestone it is 89.2. Atmospheric oxygen contains a slightly higher ratio of $\text{O}^{18}/\text{O}^{16}$ than does fresh lake water. Omitting details, differences in isotopic abundance ratios have also been reported in the elements argon, helium, and chlorine.

The abundance ratio of the isotopes of an element may be measured in the mass spectrograph either by the intensities of the lines in the mass spectrum as recorded on the photographic plate or by the strength of an electric current (ion current) produced by the flow of positively charged ions as recorded on an electrometer (Fig. 1-8). The determination of abundance ratios for the various elements is, at present, one of the most important uses of the mass spectrograph. The values for isotopic abundance are usually expressed as percentage; e.g., the abundance of the three isotopes of silicon, as given in the preceding section, are 92.27, 4.68, and 3.05 per cent, respectively. It is beyond the scope of this book to publish data of this nature, especially since investigations along this line have not been completed. The reader, if interested, is referred to the report published by the National Research Council in 1951.¹

1-18 The Isotopic Constitution of the Elements. Over 1,000 isotopes, natural and artificial, have been identified of the known elements. Of this number approximately 320 occur in nature, of which at least 40 are radioactive. For the present we shall confine our discussion to the stable, naturally occurring isotopes of the various elements. Later, in Chap. 8, we shall examine the radioactive isotopes in some detail. However, we should add that, of the more than 280 so-called "stable" isotopes, 3 are radioactive and 6 or 7 exhibit feeble radioactivity; the first 3 are Th^{232} , U^{235} , and U^{238} ; and the latter 6 or 7 are K^{40} , Rb^{87} , In^{115} , Sm^{152} , Lu^{176} , Re^{187} , and possibly V^{50} . In Table 1-6 are listed the mass numbers of the naturally occurring stable isotopes of the elements.

An analysis of the figures in Table 1-6 reveals certain facts and relationships relevant to the structure and stability of the atomic nucleus. Some of these items have been mentioned before, but they will be restated in the form of rules, for the purpose of emphasis:

1. *The masses of all stable nuclei are, except for H^1 and H^3 , never less than twice their atomic numbers.* Among the lighter elements, up to calcium, the mass number is usually twice the atomic number, indicating that the nucleus is composed of equal numbers of protons and neutrons. Beyond calcium the ratio of neutrons to protons increases, but for naturally occurring isotopes this ratio rarely exceeds 1.2.

¹ Bainbridge and Nier, *op. cit.*

TABLE 1-6 MASS NUMBERS OF THE STABLE ISOTOPES OF THE ELEMENTS

Element	Atomic number	Mass numbers, in order of abundance
H	1	1, 2
He	2	4, 3
Li	3	7, 6
Be	4	9
B	5	11, 10
C	6	12, 13
N	7	14, 15
O	8	16, 18, 17
F	9	19
Ne	10	20, 22, 21
Na	11	23
Mg	12	24, 25, 26
Al	13	27
Si	14	28, 29, 30
P	15	31
S	16	32, 34, 33
Cl	17	35, 37
A	18	40, 36, 38
K	19	39, 41, 40
Ca	20	40, 44, 42, 43, 48, 46
Sc	21	45
Ti	22	48, 46, 47, 50, 49
V	23	51, 50
Cr	24	52, 53, 50, 54
Mn	25	55
Fe	26	56, 54, 57, 58
Co	27	59
Ni	28	58, 60, 62, 61, 64
Cu	29	63, 65
Zn	30	64, 66, 68, 67, 70
Ga	31	69, 71
Ge	32	74, 72, 70, 73, 76
As	33	75
Se	34	80, 78, 76, 82, 77, 74
Br	35	79, 81
Kr	36	84, 86, 82, 83, 80, 78
Rb	37	85, 87
Sr	38	88, 86, 87, 84
Y	39	89
Zr	40	90, 92, 94, 91, 96
Nb	41	93
Mo	42	98, 96, 95, 92, 97, 94, 100
Tc	43	None
Ru	44	102, 104, 101, 88, 100, 96, 98
Rh	45	103
Pd	46	106, 108, 105, 110, 104, 102
Ag	47	107, 109

44 Fundamental Concepts of Inorganic Chemistry

TABLE 1-6 MASS NUMBERS OF THE STABLE ISOTOPES OF THE ELEMENTS (Continued)

Element	Atomic number	Mass numbers, in order of abundance
Cd	48	114, 112, 110, 111, 113, 116, 106, 108
In	49	115, 113
Sn	50	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
Sb	51	121, 123
Te	52	130, 128, 126, 125, 124, 122, 123, 120
I	53	127
Xe	54	129, 132, 131, 134, 136, 130, 128, 126, 124
Cs	55	133
Ba	56	138, 137, 136, 135, 134, 130, 132
La	57	139
Ce	58	140, 142, 138, 136
Pr	59	141
Nd	60	142, 144, 146, 143, 145, 148, 150
Pm	61	None
Sm	62	152, 154, 147, 149, 148, 150, 144
Eu	63	151, 153
Gd	64	158, 160, 156, 157, 155, 154, 152
Tb	65	159
Dy	66	164, 162, 163, 161, 160, 158, 156
Ho	67	165
Er	68	166, 168, 167, 170, 164, 162
Tm	69	169
Yb	70	174, 172, 173, 171, 176, 170, 168
Lu	71	175, 176
Hf	72	180, 178, 177, 179, 176, 174
Ta	73	181
W	74	184, 186, 182, 183, 180
Re	75	187, 185
Os	76	192, 190, 189, 186, 187, 184
Ir	77	193, 191
Pt	78	195, 194, 196, 198, 192
Au	79	197
Hg	80	202, 200, 199, 201, 198, 204, 196
Tl	81	205, 203
Pb	82	208, 206, 207, 204
Bi	83	209
Th	90	232
U	92	238, 235

2. *Elements with even atomic numbers (protons) are more abundant, more stable, and richer in isotopes than those of odd atomic numbers.* Not only does this rule hold true for the number of nuclei, but also for their percentage of abundance in nature. Of additional interest in connection with this rule is the fact that those elements whose existence in nature

has been questioned, namely, technetium, promethium, astatine, and francium, all have odd atomic numbers.

3. *Elements with even atomic numbers may have numerous stable isotopes but only one or two with odd mass numbers. If two isotopes with odd mass numbers do exist, they will differ by two mass units.* The one exception to this rule is the occurrence of three stable tin isotopes with odd mass numbers, ${}_{50}\text{Sn}^{115}$, ${}_{50}\text{Sn}^{117}$, and ${}_{50}\text{Sn}^{119}$.

4. *Nuclei composed of even numbers of neutrons are more abundant, more stable, and richer in isotopes than those with odd numbers of neutrons.* This rule is a corollary of rule 2, and it might be advantageous to consider the two rules collectively. Thus, it is possible to classify nuclei according to whether they contain even or odd numbers of protons and neutrons. Under such a classification there are four possible types of nuclei. These four types, their distribution, and abundance in nature are given in Table 1-7.

TABLE 1-7 TYPES OF NATURALLY OCCURRING STABLE ISOTOPES AND THEIR ABUNDANCE*

Constitution of nucleus		Number of stable isotopes	Abundance, %, in earth's crust
Neutrons	Protons		
Even	Even	162	87.4
Even	Odd	52	10.8
Odd	Even	56	1.8
Odd	Odd	4	0.0007

* Table does not include radioactive isotopes.

5. *Stable nuclei with even mass numbers have an even number of protons and an even number of neutrons.* As indicated in Table 1-7, there are four exceptions to this rule, ${}^1\text{H}^2$, ${}^3\text{Li}^6$, ${}^5\text{B}^{10}$, and ${}^7\text{N}^{14}$, all of which are very light nuclei where large fluctuations in binding energy may be expected (Fig. 1-1). The isotopes ${}^{23}\text{V}^{50}$ might also be added to these exceptions, but this isotope is probably radioactive.

6. *Elements with odd atomic numbers (protons) have only one or two stable isotopes.* The mass numbers of these elements are always odd, and if there are two isotopes, their mass numbers differ by two units. The only exceptions to this last statement are the five odd-odd nuclei indicated under rule 4. In these five exceptions the mass numbers of the isotopes differ by one unit.

7. *An element with an odd mass number is represented by only a single stable nucleus with an odd atomic number.* No exceptions to this rule are known. An example is fluorine, with a mass number of 19 and an atomic number of 9.

46 Fundamental Concepts of Inorganic Chemistry

8. *The number of isotopes of an element and their range of mass numbers apparently have definite limits.* Since the atomic number (number of protons) determines the chemical properties of an element and these properties are not altered by the addition of neutrons, there is no arithmetical reason why neutrons may not occur in indefinite numbers within the nucleus, to produce any number of isotopes. However, the largest number of isotopes for an element, known for a certainty, is 10 in the case of tin. The exact limit for neutron addition is not known, but the theory of a shell structure for the nucleus (Sec. 1·9) postulates that definite numbers of protons and neutrons are required to fill certain energy levels within the nucleus.

1·19 Isotopes, Isobars, Isotones, and Isomers. Originally the meaning of the term isotope was unambiguous, but with the discovery of the existence of other nuclear species it is sometimes given a wider and looser meaning than was originally intended. The shifting of the meaning from an exact term with a specific definition to a more generalized expression is unfortunate. For this reason we shall redefine the word isotope and list with explanations those other atomic species which are sometimes improperly described as isotopes in an unrestricted interpretation of the term.

Isotopes are atoms of the same element whose nuclei contain the same number of protons but different numbers of neutrons. Also by definition we know that the atomic number of an element is the number of protons in the nucleus; therefore isotopes of the same element have the same atomic number. Furthermore, we know that the chemical properties of an element are dependent upon its atomic number, and not upon any other variable factor. Consequently isotopes of the same element may vary in mass number, but they have the same atomic charges and the same chemical properties.

Isobars are atomic species having the same mass number but different atomic numbers (protons). A few examples are $^{76}_{32}\text{Ge}$ and $^{76}_{34}\text{Se}$; $^{130}_{52}\text{Te}$, $^{130}_{54}\text{Xe}$, and $^{130}_{56}\text{Ba}$; $^{210}_{81}\text{Tl}$, $^{210}_{82}\text{Pb}$, $^{210}_{83}\text{Bi}$, and $^{210}_{84}\text{Po}$. As indicated by these symbols, isobars are atoms of different elements and therefore have different physical and chemical properties. The atoms simply happen to have the same mass.

Isotones are atoms having the same number of neutrons but different mass numbers. In other words, the variable factor in the nuclei of these atoms is the number of protons (atomic number); consequently such atoms have different chemical and physical properties. For example, $^{30}_{14}\text{Si}$, $^{31}_{15}\text{P}$, and $^{32}_{16}\text{S}$ are isotones, since each of these atoms contains 16 neutrons in its nucleus.

Isomers are atomic species with the same mass number and the same atomic number but with different radioactive properties. Atoms of this

description are believed to have nuclei which are composed ultimately of the same number of protons and the same number of neutrons but which differ in their energy levels. The different energy states result from a variable arrangement of protons and neutrons in the shell structure of the nucleus, thereby producing dissimilar radioactive properties. A pair of nuclear isomers occurring in nature is uranium X₂ and uranium Z, which are found in the uranium-radium decay series (Chap. 8). These isomers are identical in that both have an atomic number of 91, both have a mass number of 234, and both are atoms of protactinium.

THE SEPARATION OF ISOTOPES

Early attempts toward the separation of isotopes were motivated by theoretical interests and met with indifferent success. The examination of nonradioactive elements, notably neon, by Thomson's parabola method (Sec. 1-14) demonstrated that isotopic species were separable. It will be recalled that, in connection with this same method, Aston partly separated neon into two fractions of different atomic weights by repeated diffusion. Historically this was the first successful attempt at isotopic concentration. These and other experiments which followed demonstrated the feasibility of utilizing variation in mass as a means of isotopic separation. However, the early methods, involving inadequate equipment, laborious effort, and small amounts of materials, resulted, at best, in only a slight enrichment of isotopic species. It was not until the discovery, in 1939, that U²³⁵ was a fissionable material and, as later revealed, capable of a chain reaction, that sufficient impetus was attained to develop and to explore the possibilities of isotopic separation with improved macromethods.

Beginning with 1939, and in succeeding years, scientists were early in recognizing that the scarce isotope, uranium-235, is the key material for the production of destructive atomic weapons and for the utilization of nuclear power. Therefore the stimulus of war-nurtured research produced greater strides in the development of effective methods for isotopic separation than might normally have been expected.

Despite the fact that the incentive for developing efficient macromethods for isotopic separation was provided by military exigencies, it is quite likely that the contributions to human welfare resulting from the use of isotopes will outweigh their use in preparing destructive weapons. The most important applications of isotopes are as tracers in investigating some of the fundamental problems in the various sciences. The characteristic property of a particular isotope is its mass or, for a radioactive isotope, its radioactivity. Either of these properties may serve as a "label" or a "tag" permitting the isotopic species to be followed through

48 Fundamental Concepts of Inorganic Chemistry

a series of chemical or physical changes. Not only is tracer research important to the chemist in following the course of a chemical reaction or in establishing the chemical constitution of a compound, but it is of even greater importance to the biologist and physiologist in their investigations of metabolic processes. The possibilities of use for isotopes as tracer elements are too numerous to mention here, but a partial survey of these uses is to be found in Chap. 8.

1-20 Factors Affecting the Separation of Isotopes. By definition the isotopes of an element vary in mass but not in chemical properties. It would appear, therefore, that the only methods which might be applied to isotopic separation would be physical methods depending entirely on properties related to mass. We shall find later that this interpretation is not entirely true, inasmuch as isotopes can also be separated by chemical means. This does not imply that isotopes of the same element can differ chemically, but rather that there are slight differences in their reaction rates. Chemical-exchange methods are discussed in Sec. 1-28.

The theoretical principles which can be put into practice to produce separation among particles upon the basis of mass alone are few in number. Obviously they must be related to the physical properties of the particles themselves. One such property is that of motion, which is related to mass in terms of kinetic energy. In this relationship kinetic energy is defined as $\frac{1}{2}mv^2$, where m is the mass and v is the speed of the particle. Thus in a gas composed of a mixture of two isotopes the average kinetic energy of the light molecules and of the heavy ones is the same. Accordingly, if the average kinetic energies are the same, the average speeds of the lighter molecules must be greater than those of the heavier molecules. Consequently any process depending upon the average speed of molecules should produce separation in particles varying in mass. The separation factor in such a process will always be small because the average speed is inversely proportional to the square root of the mass and mass differences between isotopes, except for the very light elements, are always slight.

Atoms and molecules are subject to gravitational fields, and the gravitational force acting upon a particle is proportional to its mass. We know that the heavier molecules of the atmosphere are, in proportion, more highly concentrated at lower levels than the lighter molecules, but the earth's gravity alone is quite ineffectual in producing any appreciable separation. Pseudogravitational forces of large magnitude may be secured by means of a high-speed centrifuge, and, in theory, this method of separation should be quite effective.

Particles existing in a gaseous form may be ionized by subjecting them to an electric discharge, and the movement of the resulting ions can be influenced by electric and magnetic fields. This principle is employed

in the mass spectrograph, and when the process is converted from a microgram to a kilogram basis, it becomes an effective method for separating isotopes.

Isotopes of the same element may differ appreciably in their chemical reactivities. The difference is more pronounced among isotopes of the lighter elements, as, for example, hydrogen and deuterium. Furthermore the slight variation in chemical reactivity affects the reaction rates of isotopic molecules. If two isotopic forms of an element were equally reactive, the equilibrium constant of a reaction involving both isotopes would be unity. However, the fact that the reactivities are different results in equilibrium constants which are not unity. Thus it is possible, in certain cases, for an isotope of a light element in chemical combination to exchange with another isotope of the same element in another chemical compound. If the equilibrium constant of the reaction is not unity, the reaction may be utilized for the concentration or separation of isotopes. Such reactions are designated as *chemical-exchange reactions*, and they form the basis for the most widely used method of concentrating isotopes. Various chemical-exchange reactions resulting in isotopic separations are given in Sec. 1-28.

Although a number of methods for the separation of isotopes are described in this chapter, there are only four factors to be considered in devising a separation process. These factors, which have been discussed in the preceding paragraphs, are enumerated again as follows: (1) at a given temperature, gaseous molecules, regardless of mass, have the same average kinetic energy; (2) the gravitational or centrifugal forces acting upon a particle of matter are directly proportional to its mass; (3) the electric or magnetic forces affecting ionized atoms or molecules follow Coulomb's laws for these forces; (4) among the lighter elements isotopic species may vary slightly in their chemical reactivities.

1-21 The Separation Factor. The extent to which a mixture of two isotopes may be separated in one stage of a particular process is called the *separation factor*. It is a ratio of the relative concentration of the desired isotope after processing to its relative concentration before processing. The factor, therefore, is a quantitative value for a one-stage process indicating the efficiency of the separation. In mathematical notation, if n_1 and n_2 are the numbers (or moles) of light and heavy species in a mixture before processing and N_1 and N_2 are the corresponding quantities after processing, in a one-stage process, the separation factor s may be indicated as

$$s = \frac{N_1/N_2}{n_1/n_2}$$

The size of the separation factor indicates the effectiveness of the sepa-

50 Fundamental Concepts of Inorganic Chemistry

ration. Usually this factor is only slightly greater than unity, and consequently a useful separation process is a composite of many single separation stages. In such a case the separation factor is s for each stage, and if the entire process consists of x stages, then the over-all separation factor is expressed as s^x . Several thousand stages are sometimes necessary for effective separation of isotopic species.

1.22 The Gaseous-diffusion Method. In Sec. 1.20 it was pointed out that the average kinetic energy of all molecules is $\frac{1}{2}mv^2$ at a given temperature; therefore two different molecules with masses m_1 and m_2 will have velocities v_1 and v_2 , and the kinetic energy of one molecule is equal to that of the other, as indicated by the equation

$$\frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$$

The equation may be rearranged as follows

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

This is a mathematical statement of Graham's law of diffusion, discovered in 1892, which states that *the rates at which different gases diffuse at the same temperature are inversely proportional to the square roots of their densities*. In the above equation *mass* is substituted for *density*, since the two terms are directly proportional to each other.

The word *diffusion* may be used to describe the passage of gases through a porous barrier. Accordingly, from Graham's law of diffusion, it may be deduced that a light gas will diffuse, or pass through a porous barrier, more rapidly than a heavy one. This principle was the basis for Aston's partial separation of the isotopes of neon in 1913. Later, between 1916 and 1921, W. D. Harkins at the University of Chicago applied the same principle of gaseous diffusion in an attempt to separate gaseous HCl into two fractions containing enriched proportions of the two isotopes of chlorine, Cl^{35} and Cl^{37} . Five years after attacking the problem, he reported the separation of a heavy fraction with an atomic weight 0.055 greater than that of ordinary chlorine.

Theoretically the rate of diffusion of an ideal gas through an ideal porous barrier is inversely proportional to the square root of its mass. If a gas consisting of two isotopes passes through a barrier into an evacuated container, the lighter isotope diffuses more rapidly than the heavier and, for a very short period of time, the relative concentration of the lighter isotope in the container is greater than on the other side of the barrier. For example, if hydrogen gas containing a mixture of protium and deuterium, H_2 and D_2 , is passed through a barrier, the separation factor is

$$s = \sqrt{\frac{4}{2}} = 1.414$$

However, if the process is allowed to continue indefinitely, equilibrium will be established, and the composition of the gas will be the same on both sides of the barrier. Even though the diffusate (the gas passing through the barrier) is removed from the container by means of a pump, the relative amount of the heavier isotope passing through the barrier will increase, since the gas is progressively being impoverished of the lighter isotope. Successful separations have been accomplished by using

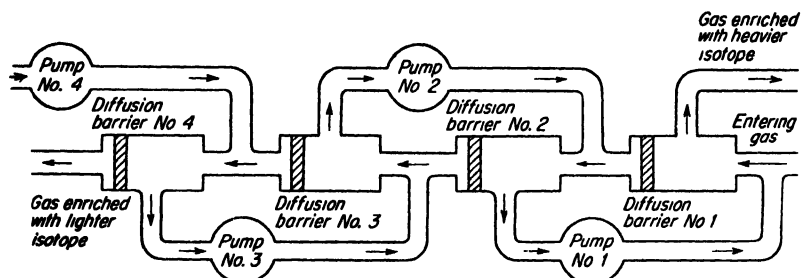


Fig. 1-11 Diagrammatic representation of the Hertz cascade system for the separation of isotopes by diffusion.

a cascade (many successive diffusion stages) in which only one half of the gas passing through the barrier of any given stage is passed along to the next higher stage, the other half being returned to the earlier stage (Fig. 1-11). This removal of one-half of the diffusate for recycling represents a compromise for those factors involving the quantity of gas permitted to diffuse, the time required to reach equilibrium, the extent of impoverishment of the gas by removal of the lighter isotope, and the over-all enrichment factor per stage for the entire process.

The efficiency of the diffusion process was greatly increased by G. Hertz¹ in 1932. By incorporating the porous barriers in series with a large number of mercury-diffusion pumps he employed a recycling process which avoided some of the difficulties inherent in the Harkins procedures. The pumping and diffusing units, operating under reduced pressures, were so arranged that the heavier and lighter constituents accumulated at opposite ends of the system. The first Hertz system, utilizing 24 pumps, separated neon into two fractions which differed by 1.4 units of atomic weight. Later, a 50-pump system produced two fractions of neon, Ne^{20} and Ne^{22} , which were spectroscopically pure, and accomplished a complete separation of protium and deuterium. Figure 1-11 is a diagrammatic representation of the Hertz system, showing four diffusion units within the multiunit process. If we consider these four units as a process for separation, then the original gas enters at the lower

¹ G. Hertz, *Z. Physik*, **79**: 108 (1932).

52 Fundamental Concepts of Inorganic Chemistry

right and the pumping system is so designed that only one half of the gas passes through barrier No. 1. The other half returns to mix with the entering gas. The diffusate, slightly enriched with the lighter isotope, passes on to barrier No. 2. Again, only one half of the gas is permitted to pass through the diffusion barrier, the other half being recycled back to the gas entering barrier No. 2. The diffusate from barrier No. 2 is passed on to diffusion barrier No. 3, where the pumping system again divides the gas into halves, one half being diffused through the barrier and the other half being recycled. This process is continued through all the diffusion stages, each diffusate being slightly enriched with the lighter isotope. The Hertz process used a closed system, so that after a period of operation an equilibrium condition was reached with the gas enriched in the lighter isotope collected at one end of the system and the gas enriched in the heavier isotope accumulated at the other end. In this process the total separation factor increases exponentially with the number of units, so that, theoretically, any degree of separation can be obtained by adding sufficient units.

As has been mentioned before, the key material for the production of atomic weapons and the development of nuclear power is the fissionable isotope of uranium, U^{235} . Uranium, as it occurs in nature, contains three isotopes, U^{238} , U^{235} , and U^{234} , and the values of their abundance are 99.3, 0.7, and 0.006 per cent, respectively. The amount of the 234 isotope is so small that it can be ignored, but most uses of uranium require that it be considerably enriched in the 235 isotope. For the preparation of nuclear weapons the fissionable material must be practically pure. Consequently one of the major engineering problems has been the development of a system, or systems, for isolating U^{235} from natural uranium. Since uranium combines with fluorine to form uranium hexafluoride, UF_6 , which, although a solid at room temperature, is vaporized at atmospheric pressure above $56^\circ C$, it is obvious that one of the first methods to be used for the enrichment of U^{235} is that of fractional diffusion. Moreover, the fact that fluorine has only a single isotope, F^{19} , reduces the separation process of the uranium hexafluoride gas to the isotopes of uranium.

The molecular weights of the two isotopic forms of uranium hexafluoride are 352 and 349; therefore, the maximum separation factor for a diffusion stage is

$$s = \sqrt{\frac{352}{349}} = 1.0043$$

As has been explained earlier in this section, the maximum diffusion factor can never be realized, and, in practice, it has been found that maximum efficiency is obtained by using a cascade system and recycling one-half of the gas from each stage back to the previous stage. The first experimental separation of uranium hexafluorides by E. T. Booth,

H. C. Paxton, and C. B. Slade, at Columbia University, indicated that the actual separation factor was approximately 1.0014. Upon a basis of this revised value it would require approximately 4,000 diffusion stages to produce 99 per cent pure $U^{235}F_6$ from uranium hexafluoride derived from natural uranium.

A gaseous-diffusion plant with this many stages must of necessity be a huge, sprawling structure. The one built by the government at Oak Ridge, Tenn., during World War II covers an area of over 100 acres and is approximately four stories high. It requires a power plant supplying nearly $\frac{1}{4}$ million kw of power and steam. The cost of the entire installation was about 500 million dollars. In spite of the enormous size of this plant its output, in terms of weight, is comparatively small. The handling of large volumes of gases at low pressures necessitates a large-volume process, but when the gaseous product is converted into terms of weight, the value must necessarily be small. In addition to the disadvantage of the large-volume process with a small weight yield the engineering problems of handling a highly reactive, poisonous, and corrosive gas made necessary the development of special pumps, nonreactive lubricants, and noncorrosive diffusion barriers. It might be added that the barriers not only had to be corrosion-resistant but also had to be mechanically strong, and uniform as to their pore structure. To ensure true diffusion, the diameter of the holes in the barriers had to be less than one-tenth the mean free path of the molecules. Or, in other words, the pores could not be larger than one-tenth of the average distance that a gas molecule travels before it collides with another molecule. The maximum size permitted for these holes was calculated as being approximately one-millionth of a centimeter in diameter.

The huge diffusion plant at Oak Ridge, Tenn., was put into successful operation before the summer of 1945. It represents one of the greatest technical achievements in the history of mankind. This particular plant was designed and built for the purpose of separating the isotopes of uranium; yet, if the necessity should arise, there is no reason why the same general process could not be utilized for the separation of the isotopes of other elements.

1.23 The Electromagnetic Method. The principle of the electromagnetic method for the separation of isotopes was given in Sec. 1.14 with the descriptions of the first mass spectrographs. In fact the electromagnetic method is simply the utilization of a giant mass spectrograph for the separation of appreciable quantities of isotopes. An oversimplification of the method would be to describe it as a macroseparation of isotopes, using essentially the principle of the early Dempster mass spectrograph. The electromagnetic method was the first to yield appreciable amounts of U^{235} for experimental purposes in the early stages of

54 Fundamental Concepts of Inorganic Chemistry

the wartime atomic-energy project. In the electromagnetic method of separating U^{235} and U^{238} a salt of uranium containing the two isotopes is vaporized and passed through an electric arc which produces positively charged uranium ions. The ions are accelerated by an electric field and converted, by means of slits, into a beam. A simplified sketch of the principles of electromagnetic separation is given in Fig. 1-12. The beam

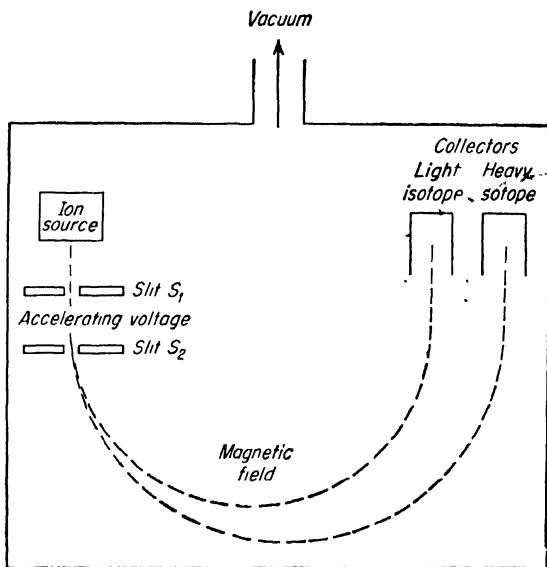


Fig. 1-12 Separation of isotopes by the electromagnetic method.

of ions is directed into a magnetic field produced by the poles of a powerful electromagnet. The ions have practically the same kinetic energy, but since the two isotopes differ in mass, their resulting ions also differ in this respect. As a result of mass differences the ions of the lighter isotope move faster than those of the heavier one. Within the magnetic field all ions are forced into curved paths, but the curved paths are of different radii, depending, again, upon mass. As can be seen from Fig. 1-12, the lighter ions are affected more by the magnetic field than the heavier ones and therefore follow paths of greatest curvature. Suitable containers are placed at the proper locations to collect the separated isotopes. The entire process is carried out in a high vacuum.

The electromagnetic method has a high separation factor, but the operation is not so simple as the description and the sketch might lead one to believe. In developing this process three limitations as to the amount of material that could be handled were encountered: First it is difficult to

produce a large quantity of gaseous ions, and if they are produced, the actual weight of material in the total volume of the gaseous ions will be small. Second, in producing the narrow beam by means of a slit system, only a small fraction of the total ions can be utilized. Third, as the quantity of material in the beam is increased, there is a corresponding increase in space-charge effects which interfere with the separating action. The first large-scale research attempt to improve the design of this method in such a manner as to minimize the foregoing limitations was performed by E. O. Lawrence and his coworkers at the University of California. His first apparatus was built around a 37-in. electromagnet removed from a cyclotron, and was called a *calutron*, a contraction of *California University cyclotron*. It is interesting to note that the huge electromagnetic separators now in use at Oak Ridge, Tenn., are still referred to as *calutrons*. With his experimental apparatus Lawrence was able to overcome the early limitations of the method and also to prove that this method was entirely feasible for efficient separation of isotopes. Construction of the first large-scale electromagnetic units at Oak Ridge began in March, 1943, and they were ready for operation in November, 1943. It was soon realized that the efficiency of the method could be greatly increased if an enriched material were fed into the units. Thus, in the summer of 1944, a thermal-diffusion separation plant was built to furnish enriched feed material for the electromagnetic process and thereby increase the over-all rate of production of pure uranium-235.

On a commercial scale this process requires enormous amounts of electric power, and complex electrical and mechanical equipment are necessary for its control. The electromagnetic plant at Oak Ridge consists of 175 buildings, which cost more than 300 million dollars. In addition the electromagnets were wound with more than 11,000 tons of pure silver, valued at approximately 400 million dollars. Therefore this plant actually cost more than the gaseous-diffusion plant. The large electromagnetic separators are no longer used for separating isotopes of uranium but are now utilized for the separation of isotopes of a large number of elements throughout the periodic table. Since many elements contain several isotopes, it is often necessary to use more than the two collecting containers indicated in Fig. 1-12. A large number of isotopes are now available for research purposes, and it is possible, as was stated in the introduction to this subtopic, that the results from the use of these tracer isotopes, in solving problems bearing on life processes, may more than repay the cost of building the electromagnetic separation units.

1-24 The Thermal-diffusion Method. The kinetic theory of gases has unduly occupied the attention of theoretical chemists and physicists over an extensive period in the development of the modern concepts of science. It is perhaps for this reason that the mathematical theory underlying the

56 Fundamental Concepts of Inorganic Chemistry

thermal-diffusion method was worked out by D. Enskog of Sweden and S. Chapman of England prior to 1920. Upon theoretical principles Enskog predicted that the application of a temperature gradient to a gaseous mixture of molecules of different masses should cause a small gradient in the relative concentrations of the components. According to this theory the heavier molecules should tend to diffuse toward the region

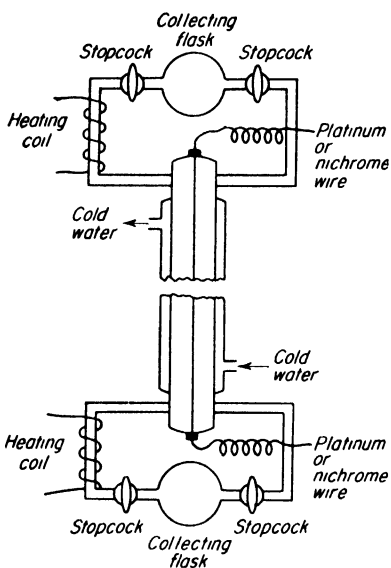


Fig. 1-13 Sketch of thermal-diffusion apparatus for separation of isotopes.

of lower temperature and the lighter molecules to the region of higher temperature. These two movements should continue until the thermal-diffusion process is counterbalanced by the effect of ordinary diffusion. Chapman had suggested that thermal diffusion might be used to separate isotopes. He even went so far as to work out, on a theoretical basis, the separation factor for the two isotopes of neon if this gas were placed in a vessel consisting of two bulbs connected by a tube, the two bulbs being maintained at certain definite, but different, temperatures.

The possibility of isotopic separation by means of thermal diffusion was elevated from mathematical speculation to practical importance in 1938 by the experiments of K. Clusius and G. Dickel¹ in Germany.

Their apparatus consisted of a vertical

tube, about 3 m in length and 1 cm in diameter, cooled by water on the outside and with a heated platinum wire along the inner axis. Figure 1-13 is a schematic representation of a thermal-diffusion column. By means of this apparatus they discovered that, not only does thermal diffusion take place as predicted by theory, but convection currents, naturally caused by the temperature gradient, instead of hindering the fractional separation actually assisted it to a remarkable degree. Using a temperature difference of 600°C between the wire and the outer surface of the tube, they were able to report definite separation of both the neon and the chlorine isotopes.

¹ K. Clusius and G. Dickel, *Naturwissenschaften*, **26**: 546 (1938).

centration of the light isotope around the hot wire, and ordinary convection currents carry these molecules upward. At the same time a similar process causes the accumulation of the heavy isotope near the cool surface of the tube, the molecules of which are carried by convection currents to the lower portion of the tube. Consequently, after a period of time, the gas in the upper part of the tube is enriched with the lighter isotope and that in the lower with the heavier isotope. It should be noted that the length of the column must be quite large as compared with its width; otherwise, ordinary diffusion will tend to restore the gas to a uniform concentration. Either isotopic fraction may be removed by means of two collecting flasks attached by tubing to either end of the fractionating column. The flasks are filled by heating one of the connecting tubes with a heating coil. This continues the convective circulation from the column into, and through, the flask.

Where a high separation factor is desired, several fractionating columns may be connected in series. In such a series the bottom of each unit is connected to the top of the next one by a closed loop of glass tubing.

The reason underlying the thermal-diffusion effect is the transfer of momentum from one molecule to another; for different gases the effect may vary widely. It is greatest for noble gases, whose molecules behave as hard spheres with short-range repulsive forces decreasing as a very large power of the inverse of the distance between atoms. The effect disappears for soft molecules, such as hydrogen chloride, with repulsive forces varying as the inverse fifth power of the distance. The method of thermal diffusion may also be applied to pure liquids or solutions, but the separation factors in these cases are usually small. Certainly the analysis of molecular attraction in liquids is extremely complicated and almost unpredictable.

As stated in Sec. 1-23, a large-scale thermal-diffusion plant was built at Oak Ridge, Tenn., during the summer of 1944 for the specific purpose of furnishing uranium hexafluoride, enriched with the U^{235} isotope, to the electromagnetic process. Uranium hexafluoride is a liquid at temperatures below 56°C , and the plant at Oak Ridge was designed for the thermal diffusion of this liquid. The thermal-diffusion process lends itself to a continuous process, but a large-capacity output cannot be attained because of the very small spacing allowed in the diffusion columns. As far as separating the isotopes of uranium, the thermal-diffusion process is much less efficient than the gaseous-diffusion method. Consequently the commercial plant at Oak Ridge was operated only for a short time. On the other hand the thermal-diffusion method seems quite ideal for isotopic enrichment on a laboratory scale, inasmuch as the apparatus is readily and cheaply constructed and needs little attention while in operation.

58 Fundamental Concepts of Inorganic Chemistry

1-25 Distillation Methods. Isotopes of the same element vary slightly in their physical properties. This variation results from nuclear mass differences and consequently is more pronounced among isotopes of the lighter elements.

The possibility of separating isotopes by means of the difference in their vapor pressures, i.e., their boiling points, was predicted by F. A. Lindemann, in 1919, upon theoretical grounds. According to this theory the surface of a liquid acts as a porous diaphragm, and the rate of escape for two or more isotopes is inversely proportional to the square root of

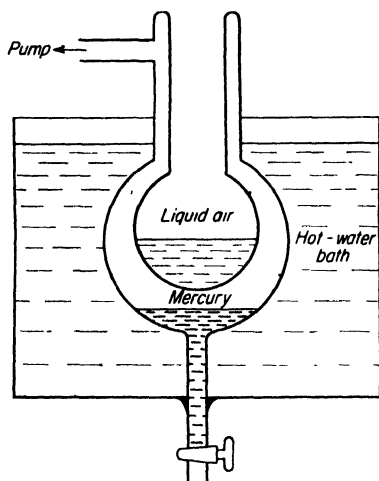


Fig. 1-14 Apparatus for separation of mercury isotopes.

their masses. Applying this theory to a method of ideal distillation, J. N. Brønsted and G. von Hevesy,¹ in 1922, achieved a slight enrichment of the isotopes of mercury. One form of their apparatus is sketched in Fig. 1-14. Mercury was evaporated in a partial vacuum at 40 to 60°C between the walls of a Dewar flask. The inner vessel was cooled with liquid air, placed about 1 to 2 cm above the mercury. This distance is approximately equal to the mean free path of the mercury leaving the surface. Under these conditions there is an absence of collisions, and all the atoms which evaporate condense on the cold surface. After about one-fourth of

the mercury had evaporated, the condensate and residue were separated. The condensate was allowed to melt and then partially evaporated again. After several fractionations in this manner a slight enrichment of the lighter isotope was to be found in the final condensate, whereas a similar enrichment of the heavy isotope occurred in the residue. The use of improved techniques, employing the same ideal distillation principle, has resulted in partial fractionation of the isotopes of chlorine, zinc, and potassium.

Enrichment of isotopes for some of the lighter elements and their compounds has been accomplished by means of efficient fractionating columns where there are sufficient differences in vapor pressures (boiling points). H. C. Urey and his collaborators obtained evidence of deuterium through the distillation of liquid hydrogen at its triple point. A slight enrichment in the concentration of O^{18} has been secured by the distillation of

¹ J. N. Brønsted and G. von Hevesy, *Phil. Mag.*, **43**: 31 (1922).

liquid oxygen. Heavy water, D_2O , boils at a temperature $1.42^\circ C$ higher than ordinary water, H_2O . The most efficient process for the enrichment of D_2O by distillation utilizes a fractionating column for a continuous process, in which an upward-directed stream of vapor is kept in contact with a downward-directed stream of liquid, the two streams constantly exchanging molecules. The molecules of H_2O have a relatively greater tendency to get into the vapor stream, and the molecules of D_2O into the liquid.

During the development of the atomic project of World War II it was at first thought that heavy water would be necessary for use as a moderator; consequently a plant for the enrichment of D_2O by distillation of water was built in 1943. However, this plant operated for less than a year, the distillation process being replaced by a more economical method of producing D_2O through a chemical-exchange reaction. Furthermore it was later learned that graphite, being a solid, was more convenient to use as a moderator, and the need for large quantities of heavy water never materialized.

1-26 The Centrifugal Method. The gravitational force acting upon atoms and molecules, tending to move them downward, is proportional to their masses. Therefore, if a mixture of two isotopes of the same element in gaseous or liquid state is subjected to a gravitational field, the heavier isotope will tend to concentrate in the direction of the field and, if there is no mixing to counteract this movement, separation will take place. The extent of separation which may be accomplished by this force is dependent upon the *mass difference* between the two isotopes, and not on their ratio. This differs from diffusion methods, where the separation factor is dependent upon the square root of the ratio of the masses. In theory it has the attractive feature that the separation is fully as effective for isotopes of the heavier elements as for the lighter ones. Accordingly a better separation should be obtained for the isotopes of U^{235} and U^{238} , with a mass difference of three units, than for the isotopes of hydrogen, protium, and deuterium, which have a mass difference of one unit. Moreover the difference between the masses of two isotopes is a constant value, and the efficiency of the separation is not affected by the molecular weight of the compound whose vapor is being subjected to gravitational force.

The centrifuge is essentially a method of applying pseudogravitational forces of large magnitude, and the possibility of separation of isotopes by its use was predicted as early as 1921 by Lindemann and Aston. However, the first experiments with the centrifuge for this purpose, by Joly and Poole, produced no positive results, probably because the speed of their centrifuge was too low. It was not until 1939 that successful enrichment of isotopes by centrifugation was accomplished. Using an

air-driven, self-balancing vacuum-type centrifuge, producing a force several hundred thousand times greater than gravity, J. W. Beams and C. Skarstrom¹ obtained an appreciable separation of chlorine isotopes, using carbon tetrachloride as the test liquid.

In the early stages of the atomic-energy project the use of the centrifuge for the separation of the U^{235} and U^{238} isotopes seemed quite promising, especially since these two isotopes have a mass difference of three units. At the suggestion of H. C. Urey tall cylindrical centrifuges with countercurrent flow were developed for this particular separation. In a centrifuge of this description a downward flow of vapor takes place at the periphery of the rotating cylinder and an upward current along its axis. Across the interface region there is a constant diffusion of both types of molecules, containing heavy and light isotopes, between the two currents of gases. Thus each molecule travels along the periphery for a short distance, then diffuses over to the axis, where it again moves for a short distance in the opposite direction. However, the radial-force field of the centrifuge acts more strongly on the heavy molecules than on the lighter ones, causing an increase in the concentration of the heavier molecules in the peripheral region. A similar concentration of the lighter molecules takes place in the axial region. The lighter isotopic species is withdrawn from the top of the cylinder, near the center, and the heavier species is removed at the bottom, near the periphery.

A pilot plant for the separation of uranium isotopes by centrifugation was constructed during the war at Bayway, N.J. Although it was operated successfully and gave approximately the degree of separation predicted by theory, no large-scale production was ever attempted. Apparently the magnitude of the engineering problems involved in erecting a large-scale production plant discouraged the development of this process.

1-27 The Electrolytic Method. This method is used only for the separation of the two naturally occurring isotopes of hydrogen. The heavier of these isotopes, with a mass number of 2, has been named *deuterium* and given the symbol D. It is the only isotope of any element to be given a special name, and this distinction arises from the fact that its physical properties are somewhat different from those of light hydrogen. The relative abundances of ordinary hydrogen and deuterium in nature are 99.9844 per cent and 0.0156 per cent, respectively.

The prediction of the existence of deuterium in nature, queer as it may seem, was the result of an unrecognized and unevaluated error in the estimation of the atomic weight of hydrogen with the mass spectrograph. Aston's value, as determined in 1927 by spectrographic means and based on the standard of O = 16.00000, was 1.00778, which was in excellent agreement with the chemically determined value of 1.00780. However,

¹ J. W. Beams and C. Skarstrom, *Phys. Rev.*, **56**: 266 (1939).

in 1929, when Giaque and Johnson discovered that oxygen existed as three isotopes, O^{16} , O^{17} , and O^{18} in the relative abundance ratios of 3,150:1:5, respectively, it became apparent that the average atomic weight of the isotopic mixture was 16.0044 (Sec. 1-16). When the chemical atomic weight of hydrogen was changed from the standard of $O = 16.0000$ to $O = 16.0044$, a value of 1.00806 was obtained, which is 0.00028 mass unit higher than that obtained by Aston with the mass spectrograph. This discrepancy could be accounted for by assuming that ordinary hydrogen contained a heavier isotope with a mass number of 2 in a concentration of approximately 1 part in 5,000. It was later learned that the error in Aston's method of estimating the atomic weight of hydrogen was greater than this discrepancy. Fortunately, unaware of this possible error, H. C. Urey began his famous and thorough search which resulted in the discovery of heavy hydrogen and for which he received the Nobel prize in 1934. In collaboration with F. G. Brickwedde and G. M. Murphy he subjected liquid hydrogen to continuous fractionation, then, by optical means, demonstrated the presence of an isotope with a mass very close to 2 within the residue.

The suggestion that isotopes might be separable by electrolysis was made as early as 1923 by J. Kendall and E. D. Crittenden, but no positive results were obtained until H. C. Urey and E. W. Washburn¹ obtained an enrichment of deuterium oxide in water by this method in 1932. Their successful experiment led to an examination of many industrial electrolytic processes in which deuterium oxide was found in various degrees of enrichment. It at once became apparent that in the electrolysis of aqueous solutions, irrespective of whether they are acid or alkaline, the lighter isotope of hydrogen is evolved more readily than the heavier one, resulting in an accumulation of the heavier isotope in the residual solution. In 1933 G. N. Lewis and his collaborators at the University of California succeeded, by the continuous electrolysis of a very large amount of water obtained from an old commercial electrolytic cell, in preparing about $\frac{1}{10}$ cc of water which contained practically only deuterium atoms of mass 2. The specific gravity of this water was about 10 per cent greater than that of ordinary water, which was in accordance with the molecular weight of D_2O .

The discovery that deuterium oxide can be produced by electrolysis stimulated considerable investigations in this field. The electrolytic production of pure deuterium and deuterium oxide is now carried out commercially in Norway, where electric power is relatively inexpensive. The current consumption is quite high; about 30,000 amp-hr is required to obtain 1 g of heavy water, which indicates that the process is feasible only where electric power is cheap and plentiful.

¹ E. W. Washburn and H. C. Urey, *Proc. Natl. Acad. Sci.*, **18**: 496 (1932).

62 Fundamental Concepts of Inorganic Chemistry

In practice the electrolysis of an aqueous solution is not a continuous decomposition, from a large volume to that of a small residual solution, because of the loss of deuterium with the gaseous products. Also, the presence of an electrolyte would prevent concentration to a very small volume. Consequently the most successful separations have employed several stages in the electrolytic process.

In the procedure most frequently used a solution of 0.5 *M* sodium hydroxide is subjected to electrolysis until it is reduced to about one-tenth its initial volume. The concentrated alkaline solution resulting from this operation is neutralized with carbon dioxide and then distilled to remove the carbonate. The enriched distillate is carried to the next stage of electrolysis, where the same procedure is repeated. A succession of electrolytic stages produces an increasing concentration of deuterium in the residual solution. After about three stages the hydrogen which is evolved in the electrolysis contains a sufficient amount of deuterium to justify the latter's recovery. This is accomplished by burning the gases and returning the condensed products to the system at the preceding stage of electrolysis. About seven stages are required to yield fairly pure deuterium oxide.

The progress of enrichment which may be expected in a succession of electrolyses is indicated in Table 1-8.

TABLE 18 CONCENTRATION OF DEUTERIUM BY ELECTROLYSIS*

Stage of electrolysis	Liters of solution electrolyzed	Density of residue, d_4^{20}	Per cent of deuterium in residue
1	2,300	0.998	0.03
2	340	0.999	0.5
3	52	1.001	2.5
4	10	1.007	8.0
5	2	1.031	30.0
6	0.42	1.098	93.0
7	0.08	1.104	99.0

* Data from H. S. Taylor, H. Eyring, and A. A. Frost, *J. Chem. Phys.*, 1: 823 (1933).

The electrolytic method has not been very successful in the separation of isotopes of elements other than hydrogen. The electrolysis of lithium salts, in successive stages, has resulted in a slight separation of the isotopes of this element. In the enrichment of deuterium oxide in water there should be, at the same time, an enrichment of the O^{18} isotope of oxygen. Such an increase in the O^{18} isotope has been verified experimentally, but the separation factor is extremely small. H. L. Johnson¹

¹ H. L. Johnson, *J. Am. Chem. Soc.*, 57: 484 (1935).

has computed that a volume reduction sufficient to convert ordinary water to a residue 99 per cent in D_2O will enrich the residue with O^{18} to the extent of only 20 ppm in the density of water. Furthermore he concludes that, if the entire ocean were reduced, by electrolysis, to a volume of 1 cc, the concentration of the heavy isotopes of oxygen would be less than doubled.

1-28 Chemical-exchange Methods. It was stated in Sec. 1-20 that the chemical properties of isotopes of the same element were, as a rule, practically identical but that in some cases there seem to be slight differences in reactivity. These differences appear as differences in reaction rates and are evident in the equilibrium constants of isotopic-exchange reactions.

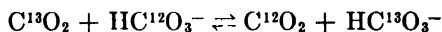
The differences in the reactivities of isotopic molecules have been ascribed to differences in the energies that such molecules possess at absolute zero. It is believed that the natural vibration frequency of atoms in a molecule depends to some extent upon the mass of the atoms involved, and this vibration frequency affects the energy of the molecule at absolute zero. This energy is frequently denoted the *zero-point energy*, and differences in zero-point energies produce differences in activation energies. It is beyond the scope of our study to explore the theoretical aspects of zero-point energies, but chemical affinity within an isotopic molecule is related to the mass of the isotope present. As might be expected, the greatest difference in chemical reactivity of any isotopes of the same element is exhibited in hydrogen and deuterium. The difference in chemical behavior of isotopes resulting from a difference in mass is called the *isotope effect*. This effect, which is notable in hydrogen and perceptible in the lighter elements, becomes very feeble or disappears in the heavier elements. For those elements in which it does appear the isotope effect may be utilized as a method for isotopic enrichment. Such a process is known as a *chemical-exchange method*.

Not only may differences in mass produce differences in chemical reactivity among isotopic atoms, but the mass of such atoms should affect both the velocity and vibrational energy of a molecule. Thus we shall have occasion to use the term *isotopic molecules*, which may be defined as molecules that are identical in chemical and structural formulas but different in their isotopic composition. Inasmuch as there is a difference in chemical reactivity among isotopic atoms, it is not surprising that there is likewise a difference in such activity among isotopic molecules containing the lighter atoms. Furthermore, at the same temperature, heavier isotopic molecules have lower velocities and undergo fewer collisions than lighter ones. This change in activity is proportional to the square root of the ratio of the masses of the molecules. Heavier molecules also require more energy for dissociation than lighter ones; therefore isotopic

64 Fundamental Concepts of Inorganic Chemistry

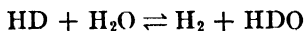
molecules may be expected to undergo chemical transformations at different rates. Consequently, if two isotopic molecules with different reaction rates are involved in a chemical reaction, the equilibrium constant for the molecular reaction will not be unity. Therefore it is possible, under certain conditions, for an isotope of a light element in chemical combination to exchange with another isotope of the same element in another chemical compound. The use of chemical-exchange reactions has become the most widely exploited of the various methods for concentrating the isotopes of the lighter elements.

In using the chemical-exchange method to produce an isotopic enrichment it is necessary to exploit an equilibrium reaction involving two isotopes of the same element, in which the isotopic distribution is not the same as would have been the case if the two isotopes had identical reactivities. For example, the equilibrium between gaseous carbon dioxide and the bicarbonate ion in sodium bicarbonate solution,



has been shown to have an equilibrium constant of 1.012 favoring the concentration of C^{13} in the bicarbonate solution. Since the concentrations of $\text{HC}^{12}\text{O}_3^-$ and C^{12}O_2 are large as compared with those containing C^{13} , they may be considered as constant; hence the ratio of $\text{HC}^{13}\text{O}_3^-/\text{C}^{13}\text{O}_2$ equals 1.012, indicating that the bicarbonate solution contains 1.2 per cent more of the C^{13} isotope than the gaseous carbon dioxide in equilibrium with it.

One of the most familiar isotopic equilibrium reactions is the one which is established between hydrogen and water. Since both hydrogen and water contain small amounts of deuterium, the equilibrium may be written as



The equilibrium constant of this reaction at 25°C is 3.703 in the direction of an increase of deuterium in water. The concentrations of H_2O and H_2 are large and can be considered as constant; therefore, the ratio of HDO/HD is 3.703, denoting that the concentration of deuterium in the water is between three and four times as great as in the hydrogen gas in equilibrium with it. The relatively high separation factor of 3.7 for this reaction indicates that it might be utilized as a means for the enrichment of the heavier isotope. One of the original objections to the use of this reaction in a chemical-exchange method for the production of heavy water was its slowness in establishing equilibrium. In the early stages of the wartime atomic-energy project it was thought that large quantities of heavy water would be necessary for use as a moderator. This anticipated need stimulated a search for a suitable catalyst to speed the attain-

ment of equilibrium in the isotopic reaction between hydrogen and water. Such a catalyst was discovered, and a plant for the production of heavy water, utilizing this reaction, was built in British Columbia, Canada.

The chemical-exchange method for producing heavy water turned out to be superior to the electrolytic process in terms of efficiency and power consumption. In this process water flows, from the top of a tower containing a catalyst, downward to meet a mixture of steam and hydrogen moving upward. The catalyst promotes a rapid isotopic exchange reaction between the hydrogen and the water molecules in the steam; and, as indicated by the large separation factor, there is a concentration of deuterium in the steam in the form of D_2O molecules. The flow of water from the top of the tower produces condensation of the steam, and the water emerging from the bottom of the tower is enriched with respect to the heavier isotope. This water is electrolyzed, and the resulting hydrogen, enriched with deuterium, is reprocessed in the system. The actual plant consists of a cascade of towers, with the largest towers at the feed end and the smallest towers at the production end. The repeated operations rapidly furnish a high concentration of D_2O at a reasonable cost.

As a general rule, whenever an isotopic atom in a gaseous substance is in equilibrium with an isotope of the same element in a liquid or a solution, the gas will have a different isotopic composition from that of the liquid. Exchange reactions involving equilibria between gas and liquid phases have been investigated more extensively than other types. Table 1-9 lists some of the most common of these reactions. The equilibrium

TABLE 1-9 ISOTOPIC-EXCHANGE EQUILIBRIA

<i>Exchange reaction</i>	<i>K, 25°C</i>
$SO_2^{16} + 2H_2O^{18} \rightleftharpoons SO_2^{18} + 2H_2O^{16}$	1.028
$CO_2^{16} + 2H_2O^{18} \rightleftharpoons CO_2^{18} + 2H_2O^{16}$	1.080
$CO^{16} + H_2O^{18} \rightleftharpoons CO^{18} + H_2O^{16}$	1.028
$O_2^{16} + 2H_2O^{18} \rightleftharpoons O_2^{18} + 2H_2O^{16}$	1.012
$ClO_2^{16} + 2H_2O^{18} \rightleftharpoons ClO_2^{18} + 2H_2O^{16}$	0.993
$Cl_2^{36} + 2HCl^{37} \rightleftharpoons Cl_2^{37} + 2HCl^{36}$	1.006
$Br_2^{79} + 2HBr^{81} \rightleftharpoons Br_2^{81} + 2HBr^{79}$	1.0008
$HCN^{15} + N^{14}H_4^+ \rightleftharpoons HCN^{14} + N^{15}H_4^+$	1.038
$HCl + DI \rightleftharpoons DCl + HI$	1.527
$S^{32}O_2 + HS^{32}O_4^- \rightleftharpoons S^{32}O_2 + HS^{36}O_4^-$	1.040

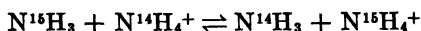
constants for chemical-exchange reactions, except those involving the very light elements, are usually so close to unity that very little concentration can be achieved by a one-stage process. Accordingly multistage processes are usually necessary to produce an appreciable enrichment of an isotopic species. One process, devised by H. G. Thode and H. C. Urey¹ for the enrichment of N^{15} , is claimed to have an efficiency 1,000

¹ H. G. Thode and H. C. Urey, *J. Chem. Phys.*, **7**: 34 (1939).

66 Fundamental Concepts of Inorganic Chemistry

times that of the Hertz cascade diffusion method. Their apparatus consisted of several glass-packed columns filled with efficient packing materials arranged in cascade, such that a smaller second column operates on the product of the first and a third column operates on the product of the second. A flow scheme for this apparatus is sketched in Fig. 1·15.

The method depends on the isotopic exchange between ammonia gas and ammonium ions in an ammonium nitrate solution, according to the equation



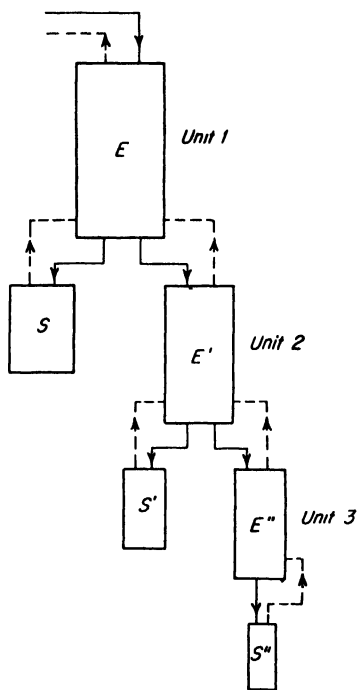
for which the equilibrium constant is 1.023. The direction of the reaction favors an increased concentration of N^{16} in the ammonium salt solution at the expense of the ammonia gas in equilibrium with it.

In this method a solution of ammonium nitrate is fed into column E of Unit 1, and $\frac{9}{10}$ of the liquid reaching the bottom is passed into a stripper column S , where ammonia gas is liberated by the addition of NaOH and returned through the feed column. Unit 2 operates on the product of Unit 1, which is $\frac{1}{10}$ of the solution arriving at the bottom of column E . As in the preceding unit, $\frac{9}{10}$ of the liquid reaching the bottom of column E' is passed into stripper S' , for regeneration of ammonia, and $\frac{1}{10}$ is fed into Unit 3. All the liquid arriving at the bottom of column E'' passes to stripper S'' , from which all the ammonia is liberated and returned through the system. With this cascade system

Fig. 1·15 Flow scheme of apparatus for the enrichment of N^{16} isotope.

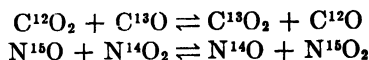
the ratio of the isotopes is changed by a factor of 1,000, and a product containing as much as 72.8 per cent N^{16} has been obtained.

Exchange reactions are not restricted to gas-liquid equilibria, and although this type seems most promising at present, other types of isotopic exchanges have been investigated. An example of a liquid-solid system is the case where alkali metal ions are exchanged in zeolites. If a solution of lithium chloride is permitted to descend through a column containing sodium zeolite, the isotopes of the lithium replace the sodium ions at a slightly different rate. The Li^6 replaces sodium ions more



readily than the Li^7 so that the solution becomes enriched in Li^7 . On the other hand, displacement of lithium ions in lithium zeolite by sodium ions removes Li^7 more rapidly, so that the zeolite becomes enriched with Li^6 .

Exchange reactions involving gas-gas systems have been utilized for the enrichment of isotopes. Conditions for the attainment of an equilibrium between two gases may be secured in gaseous-diffusion columns, and isotopic separation is achieved by arranging such columns in cascade. Two examples of exchange reactions between gaseous isotopic molecules are the carbon dioxide-carbon monoxide system and the nitric oxide-nitrogen dioxide system. The isotopic exchanges which take place in these reactions are indicated in the following equations:



EXERCISES

1. What particles are believed to make up the composition of a stable nucleus?
2. Do the particles (nucleons) within a nucleus touch each other? Explain.
3. What would be the magnitude of a force operating between a kilogram of protons located upon the sun and another kilogram of protons located on the earth, assuming that the distance between the two charges is 1.5×10^{12} cm?
4. What is the density of nuclear matter in grams per cubic centimeter?
5. What evidence do we have that the arrangement of nucleons within the nuclei of atoms is in the form of a shell structure?
6. How were neutrons first produced and recognized?
7. Describe the principle of a cloud chamber, and explain how it may be used to detect high-energy particles.
8. What is the composition of cosmic rays?
9. Frédéric Joliot-Curie once made the statement that, had he heard or read Rutherford's Bakerian Lecture of 1920, he and his wife would have identified the neutron particle. Explain this statement.
10. What is the relation between nuclear charge and atomic number?
11. A greater proportion of neutrons are present in the nuclei of heavier atoms than in lighter ones. Why is a higher ratio of neutrons to protons to be expected in heavier nuclei?
12. What were the arguments used in explaining the existence of the neutrino particle before its actual discovery?
13. In June, 1954, Marcel Schein of the University of Chicago reported the discovery of the antiproton. One of these particles struck the aluminum cover of a film pack at an altitude of 101,000 ft, producing a track upon the film. Why has this particle not been discovered earlier on the surface of the earth?
14. Explain surface-tension effect in the nucleus. How does surface-tension effect change with the size of a nucleus?
15. What is the relation between packing fraction and nuclear stability?
16. How do two isotopes of the same element differ in nuclear structure?

68 Fundamental Concepts of Inorganic Chemistry

17. What is the relation between binding energy and packing fraction of a nucleus?

18. What is the difference between isotopes and isobars?

19. What useful purposes may be accomplished by the separation of isotopes?

20. Nickel is believed to be one of the principal constituents of the earth's core. Nickel also falls near the bottom of the packing-fraction curve. Correlate these two statements.

21. Assuming that the nuclei of atoms are composed entirely of neutrons and protons, what are the numbers of each in the nuclei of H^3 , He^4 , Li^7 , K^{39} , and U^{238} ?

22. What is the packing fraction of the stable isotope of arsenic, which has an isotopic mass of 74.934 and a mass number of 75?

23. Which are the three most important methods of concentrating isotopes, and why are they more important than other methods?

24. The atomic mass of H^2 is 2.014708. What are the mass defect, the packing fraction, and the mean binding energy per particle for this atom?

25. What difficulties would be encountered in attempting to separate the isotopes of chlorine by the diffusion of chlorine gas?

26. The atomic weight of oxygen in carbon dioxide, which is in equilibrium with gaseous water, differs from that of oxygen in water by about 1 part in 100,000. Since this is true, are we justified mathematically in regarding the chemical atomic weight of oxygen as a constant of 16.0000?

27. The atomic mass of Fe^{56} is 55.9531. What are the mass defect, the packing fraction, and the mean binding energy per particle for this atom?

28. The chemical atomic weight of lithium is 6.940. The physical atomic weights of the two isotopes are 6.01697 and 7.01822. What is the isotopic composition of naturally occurring lithium?

29. The possible variations in the chemical atomic weights of lithium and chlorine, due to isotopic exchange, are approximately *one* in the last accepted figure for each of their atomic weights. More precise determinations of these atomic weights are futile. Explain the truth of the last statement.

30. The atomic mass for Th^{232} is 232.11. What are the mass defect, the packing fraction, and the mean binding energy per particle for this atom?

31. The chemical atomic weight of carbon is 12.010. The physical atomic weights of its two naturally occurring isotopes are 12.00383 and 13.00758. What is the isotopic composition of naturally occurring carbon?

32. What is the approximate density of liquid H_2O at 25°C ?

33. D_2O is commonly called heavy water, although H_2O^{17} and H_2O^{18} are heavier than H_2O^{16} . How may D_2O be distinguished from H_2O^{18} ? If D_2O and H_2O^{18} should occur as a mixture, how might they be separated?

34. When D_2O was first discovered, a somewhat fantastic theory was advanced that old age might partly be attributed to the accumulation of D_2O in the body. What possible arguments might be advanced for such a theory?

35. Describe three methods for concentrating heavy water.

36. Given that isotopes B^{10} and B^{11} have masses 10.01618 and 11.01284, respectively, and are mixed in the ordinary element in the proportion of 18.83 per cent and 81.17 per cent, respectively, calculate the chemical atomic weight of boron.

37. The chemical atomic weight of bromine is 79.916. The physical atomic

weights of its two isotopes are 78.9440 and 80.9419. What is the isotopic composition of ordinary bromine?

38. Describe how deuterium is produced commercially.

39. Calculate the relative speeds for the gaseous molecules of $U^{235}F_6$ and $U^{238}F_6$; of Ne^{20} and Ne^{22} . Which pair of the foregoing isotopes should be easier to separate by gaseous diffusion? Explain.

40. What method has been most successfully used for the separation of the isotopes of hydrogen? For the separation of the isotopes of uranium?

41. If the relative proportions of oxygen isotopes O^{16} , O^{17} , and O^{18} , are 3,150:1:5, respectively, calculate the atomic weight of O^{16} on the chemical scale.

42. What is the mass difference between the molecules $U^{235}F_6$ and $U^{238}F_6$? Between Ne^{20} and Ne^{22} ? Which pair of isotopes should be easier to separate by centrifugal methods? Explain.

43. Show that 31.0 per cent of all copper atoms have an atomic weight of 65.

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CHAPTER 2

Atomic Structure

The introduction of the atomic theory by John Dalton early in the nineteenth century marks the inception of a modern era in chemical thinking. The virtue of Dalton's theory was not that it was new or original, for theories of atoms are older than the science of chemistry, but that it represented the first attempt to place the corpuscular concept of matter upon a quantitative basis. Without reviewing or analyzing Dalton's total contributions to science it may be said that his theory in regard to the formation of chemical compounds from atoms transformed chemistry from a field of philosophical speculation to one of practical research. The theory of the atomic constitution of matter dates back at least 2,500 years to the scholars of ancient Greece, whose ideas regarding atoms have been handed down to us in the writings of Democritus. Thus we might say that as far as atomic theory is concerned Dalton added nothing new. He simply displayed a unique ability to crystallize and correlate the nebulous notions of the atomic constitution prevalent during the early nineteenth century into a few simple quantitative concepts.

EARLY THEORIES OF ATOMIC STRUCTURE

2.1 The Atomic Theory. The essentials of Dalton's atomic theory may be summarized in the following postulates:

1. *All matter is composed of very small particles called atoms.*
2. *Atoms are indestructible: they cannot be subdivided, created, or destroyed.*
3. *Atoms of the same element are similar to one another and equal in weight.*
4. *Atoms of different elements have different properties and different weights.*
5. *Chemical combination results from the union of atoms in simple numerical proportions.*

Thus, to Dalton the atoms were solid, hard, impenetrable particles,

as well as separate, unalterable individuals. Dalton's ideas of the structure of matter were borne out by a considerable amount of subsequent experimental evidence as to the relative masses of substances entering into chemical combination. Among the experimental results and relationships supporting this atomic theory were Gay-Lussac's law of combination of gases by volume, Dalton's law of multiple proportions, Avogadro's hypothesis that equal volumes of gases under the same conditions contain the same number of molecules, Faraday's laws relating to electrolysis, and Berzelius's painstaking determination of atomic weights. These overwhelming pieces of evidence forestalled any attempt to modify greatly the conceptions regarding the constitution of matter during the nineteenth century. The most notable attempt toward any modification was Prout's hypothesis that matter was made up of multiples of a fundamental substance which he suggested might be hydrogen. This idea of a primordial particle, although rapidly discredited by the accurate determinations of atomic weights, was an inspired suggestion that burdened the consciences of thoughtful scientists for over 100 years.

The methods of chemical analysis were incapable of solving the problem of the constitution of the atom, and the first step toward any solution came from an unexpected source: the study of the discharge of electricity through highly rarefied gases. Long after cathode rays had been discovered, Sir J. J. Thomson, in 1897, succeeded in proving that they consisted of particles carrying a charge of negative electricity with masses less than one-thousandth of the hydrogen atom. In this way the existence of particles smaller than atoms was proved. Moreover, since it was later discovered that these particles (electrons) could be produced in various ways, e.g., by the action of ultraviolet light on metals and by heating metals to incandescence, the inescapable conclusion was reached that the electron was a constituent of all substances. From these experiments and speculations concerning them arose the idea of the electronic structure of matter.

In 1904 Sir J. J. Thomson, elaborating upon a suggestion made by Lord Kelvin a little earlier, advanced the first definite theory as to the internal structure of the atom. According to this theory the atom was assumed to consist of a sphere of positive electricity, having embedded in it a number of electrons equal to the positive charge and arranged symmetrically in rings in accordance with the electrostatic forces operating between the opposite charges. Since the weight of the electron had been determined to be less than one-thousandth of the hydrogen atom, such a solid spherical structure implied that atoms, especially the heavier ones, must contain thousands of electrons. This theory raised more questions than it answered and, consequently, was never widely accepted.

2.2 Methods for Exploring Atomic Architecture. We have said that chemical analysis throws no light on the problem of atomic structure. On the other hand the chemical properties of atoms may indicate certain probable distributions of electrons necessary to produce such properties. This aspect of atomic structure will be examined in some detail in Chap. 4 in connection with chemical binding. The theories underlying the modern nuclear atom have been developed almost entirely by physicists from results obtained in certain physical experiments. We shall have occasion to describe, in our later discussions, some of the methods which have been most fruitful in exploring the structure of the atom; nevertheless it seems worthwhile to list these physical procedures at this point. They are:

1. The scattering of alpha and beta rays, and of X rays, by atoms and molecules
2. The atomic spectra, both in the visible and invisible regions, produced by the excitation of atoms and molecules
3. An examination of the products of natural radioactivity
4. An examination of the products resulting from the bombardment of matter with accelerated particles

Instruments for accelerating particles were not available in the early stages of the development of the concept of a nuclear atom, and therefore this method played no part in the formulation of the so-called Rutherford-Bohr "atom model."

2.3 Rutherford's Model of the Atom. Our present ideas of atomic structure are based on the atomic concept presented by Rutherford in 1911. Before describing this concept it should be noted that the idea of a nuclear atom did not originate with Rutherford, although his convincing presentation of its possibilities has justified giving him much of the credit. As far back as 1903 P. Lenard had showed that cathode rays could be made to penetrate a thin aluminum window and pass out into the air beyond. From this and other subsequent related experiments he concluded that cathode rays could pass freely through the thousands of atoms which make up the substances with which he experimented. Furthermore he deduced that the greater part of an atom must be empty. In 1904 the Japanese physicist H. Nagaoka had showed mathematically that a nuclear atom constructed on the principle of the planet Saturn would be stable, provided that the attraction of the nucleus was great and that the electrons, moving around the nucleus in rings, were in rapid motion. It is indeed unfortunate that neither the speculations of Lenard nor the calculations of Nagaoka aroused sufficient interest at the time that they were advanced for either of these two scientists to be accorded the recognition each deserved in the development of atomic theories. Thus it was that circumstances, timing, and favorable publicity conspired to such an

extent that the majority of books today give Rutherford almost complete credit for the conception of the nuclear atom.

Rutherford's atom consists of a positively charged nucleus, very small as compared with the size of the atom as a whole, surrounded by a distribution of electrons whose number equals the nuclear charge. This proposed model is sometimes compared to our planetary system with the sun as the nucleus on a macroscale. According to Rutherford most of the mass of the atom is concentrated in the nucleus. Since the number of electrons equals the nuclear charge, the atom as a whole is electrically neutral. This model resulted from conclusions drawn from experiments on the scattering of alpha particles from a radioactive source when the particles were passed through thin sheets of metal foil.

The passage of alpha particles, which are actually positively charged helium atoms, through metal foils gave the following separate pieces of information:

1. Confirmation of observations made by Lenard that matter is highly permeable to alpha particles. The presence of rays beyond the foil was detected by scintillations produced on a zinc sulfide screen. This fact indicated that the structure of the atom is largely empty space.

2. A sharply defined pencil of alpha rays, produced by passing the rays through pinholes, becomes enlarged after emerging from a metal foil. This enlargement was interpreted by Rutherford as resulting from deflections of the alpha particles by electric fields inside and around the atoms making up the foil.

3. Not only did scintillations on a zinc sulfide screen appear beyond the metal foil, but a few appeared on the impact side. Rutherford concluded that the latter scintillations could be produced only by recoil of alpha particles caused by the presence of strong positively charged fields.

From the foregoing observations it appears that the scattering of alpha particles is produced by the strong repulsive forces of the positively charged nuclei. Consequently an alpha particle suffers little, if any, deflection when passing near the electrons of an atom but will experience

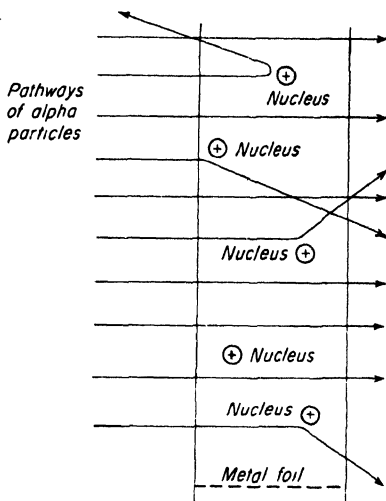


Fig. 2-1 Deflection of alpha particles by atomic nuclei upon passage through a metal foil.

74 Fundamental Concepts of Inorganic Chemistry

a large deflection when passing close to a nucleus. Moreover the recoil of an alpha particle can be produced only by close contact with a positively charged nucleus. Figure 2.1 is a sketch indicating the scattering of alpha particles in passing through metal foils.

ATOMIC NUMBERS

2.4 The Nuclear Charge. From experimental data obtained in passing alpha particles through metal foils Rutherford concluded that the atom is an open structure composed of a relatively massive, positively charged nucleus surrounded by comparatively light, negatively charged electrons. Most of the alpha particles pass unimpeded through the spaces between electrons, and any deflection caused by these particles is immeasurably small. Occasionally a positively charged alpha particle comes near a positively charged nucleus, and either electrical repulsion causes a large deflection, or the alpha particle is stopped completely and caused to reverse its direction. From the angles of deflection and the number of recoil particles Rutherford was able to calculate approximately the total amount of positive charge on the nucleus. This total positive charge is also equivalent to the number of electrons distributed around the nucleus. In all his experiments Rutherford found the number of charges on the nucleus to be equal to about one-half the atomic weight of the element. Owing to experimental difficulties and the fact that indirect methods were used in determining the number of alpha particles falling per unit of time on the metal foil, Rutherford's data were subject to a large error. Yet his conclusion that the nuclear charge is roughly half the atomic weight of the element is in striking agreement with results obtained in a number of subsequent related investigations involving the use of more refined methods.

In 1913, two years after Rutherford first proposed the nuclear atom, the Dutch physicist A. van den Breck pointed out that the atomic number of an element is equal to the number of charges carried by its nucleus. The use of the term *atomic number* goes back to the time of Newlands, who, in 1863, assigned to the elements in the order of their atomic weights a series of numbers beginning with hydrogen as 1. Accordingly the ordinal numbers of the elements, as suggested by van den Breck, indicate the number of positive charges borne by the nuclei of the respective elements.

Rutherford's conclusions and van den Breck's proposition are combined in the following statement: *The atomic number of an element is equal to the number of positive charges on, and the number of electrons distributed around, the nucleus; furthermore it is approximately equal to half the atomic weight.*

2.5 X-ray Spectra. The next important forward step in connection with the problem of atomic structure was the identification of the number

of excess positive charges on the atomic nucleus with the ordinal number (atomic number) of the element in the periodic classification. Since the advance was accomplished by photographing the X-ray spectra of various elements, some description of the apparatus used for this purpose seems pertinent at this point.

From 1896 to 1913 all X-ray tubes were of the type shown in Fig. 2-2. In this tube cathode rays (electrons) leave the cathode at right angles

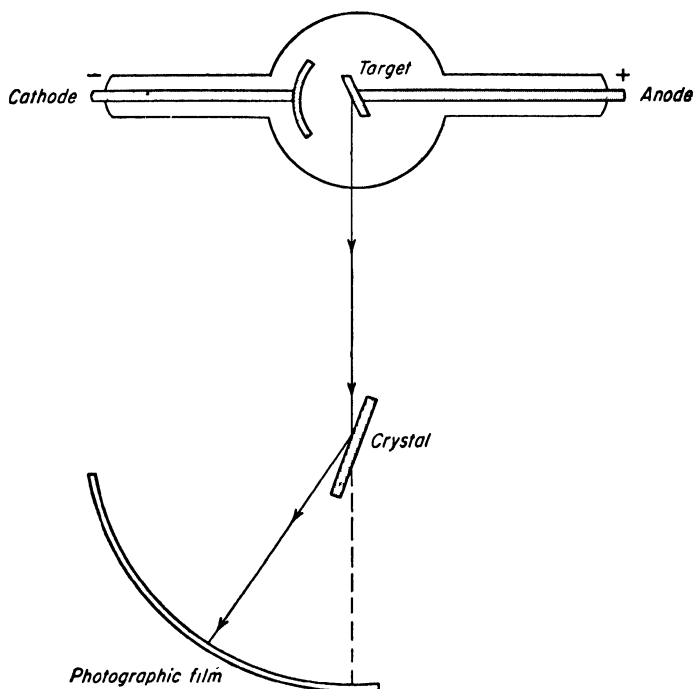


Fig. 2-2 X-ray spectrograph.

to its surface. The concave cathode permits the rays to be focused at a small spot on the metal target, which is also the anode. This spot is the center of emission for the X rays. The radiation behaves in a non-corpuseular manner, except in certain phenomena such as the Compton effect, and possesses electromagnetic characteristics analogous to light; hence, X rays are not deflected in electric or magnetic fields. However, the wavelengths of X rays are some 10,000 times shorter than visible light; therefore it is impossible to make a diffraction grating with lines close enough together to cause interference phenomena such as may be obtained in the case of light. In 1912 M. Laue conceived the idea of using the lattice of a crystal as a grating for the diffraction of X rays.

76 Fundamental Concepts of Inorganic Chemistry

This possibility results from the fact that the distance between adjacent particles in a crystal is so small that some X rays are diffracted on passing through the lattice. Moreover the major portion of the radiation penetrates matter without being deflected at all. The small amount of diffraction which is produced by the closely spaced atoms in a crystal permits the determination of the wavelength, or frequency, of the X rays, by which they may be located on the same scale as visible light.

The spectral analysis of X rays, using the diffraction effect of a crystal, was first accomplished in 1912 by W. H. and W. L. Bragg. The essentials of their X-ray spectrograph are shown in Fig. 2-2. The X rays emanating from the cathode tube are sorted into a beam by passing them through two

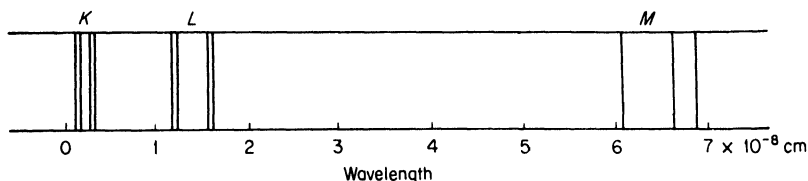


Fig. 2-3 The K, L, and M series in X-ray spectra for the element tungsten.

slits. The resulting beam strikes the surface of a salt crystal, and most of the radiation passes directly through the crystal, but a small fraction is deflected from its original path. The deflection of X rays is unlike that of visible light from a polished surface. At the glancing angle of the crystal, visible light would be deflected almost entirely from the surface, but X rays are deflected by the many planes of atoms within the lattice. When the X rays from a cathode tube are examined in this manner, it is found that the radiation is made up of two components: (1) the *scattered* radiation, which appears as a continuous band; and (2) the *characteristic* radiation, which is made up of a series of lines depending upon the nature of the anode. The two components, the band and the line spectrum, are superimposed on one another in the spectrogram.

As far as atomic structure is concerned, the characteristic radiation is of greater importance, since the system of lines produced by this component depends upon the composition of the anode. Compared with the visible spectra, the characteristic X-ray spectra are surprisingly simple. For each element used as a target it is possible to obtain a series of monochromatic X rays, which are classified according to their wavelengths into K, L, M, etc., series. These rays appear as groups of lines in the spectrogram. Figure 2-3 represents a typical spectrum for a single element.

2-6 Atomic Numbers. In 1913-1914 the young English physicist H. G. J. Moseley, working in Rutherford's laboratory at the University of Manchester, examined the X-ray spectra of 38 different elements,

beginning with that of aluminum and ending with that of gold. The apparatus he used resembled the spectrograph shown in Fig. 2-2, except that his X-ray tube contained a miniature trolley bearing a number of elements. They were so arranged that each element could be moved, when desired, into position as a target for the beam of cathode rays.

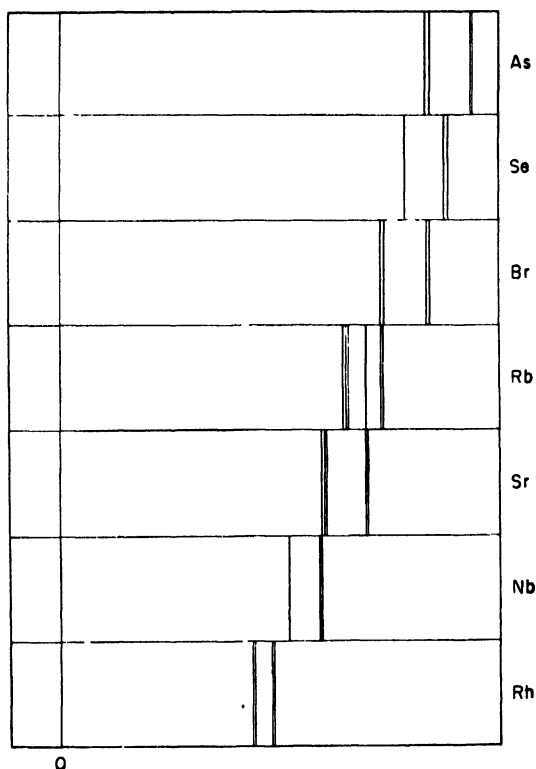


Fig. 2-4 The K series for elements As through Rh.

Where it was impractical to use a particular element as a target, e.g., as with bromine, which is a gas, the target was coated with a compound of the element. When the beam of cathode rays was allowed to impinge on each of these targets, a characteristic radiation for each was produced. The radiation was analyzed by using a crystal of potassium ferrocyanide as a diffraction grating, and the resulting rays were allowed to fall on a photographic plate.

As was stated in the preceding section, the X-ray spectrum for any particular element is quite simple. Only two lines, called the *K series*, are involved for the lighter elements, and these two lines are spaced close

78 Fundamental Concepts of Inorganic Chemistry

together. As the atomic weight of the element increases, the wavelength of the X rays decreases. In the heavier elements a second series of characteristic X-ray lines appear, known as the *L series*, and these are also displaced in the direction of shorter wavelengths as the atomic weight increases. In the heaviest elements a third series of lines, called the *M series*, are found. When the elements are arranged in the same order as in the periodic table, the wavelength of any one of the characteristic lines of the *K*, *M*, or *L* series decreases regularly with an increase in the ordinal

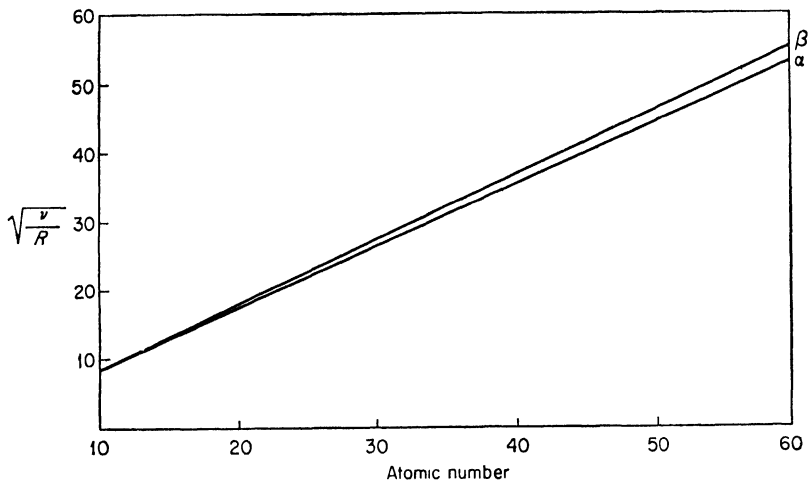


Fig. 2.5 Relation between atomic number and frequency for the *K* series in X-ray spectra. In the formula $\sqrt{\nu/R}$, *R* is the Rydberg constant.

number of the element in the periodic table. The shifting of wavelength with successive elements is shown in Fig. 2.4. This figure was adapted from a photograph made by M. Siegbahn, who repeated and extended Moseley's measurements.

The frequencies of X rays, denoted by the symbol ν , are calculated by dividing the wavelengths of the X rays, measured in centimeters, into the velocity of light. The frequency of the line belonging to any one of the X-ray series is quantitatively related to the atomic number *Z* of the element by the mathematical expression

$$\nu = a(Z - b)^2$$

where *a* is a proportionality constant and *b* is a constant for all the lines of a given series. When Moseley plotted the square root of the characteristic frequencies against the atomic number *Z* of the elements, he obtained approximately straight lines. The relation between atomic number and frequency for the *K* series is shown in Fig. 2.5. Upon the

analysis of his measurements and calculations, Moseley concluded, and we use his own words: “. . . there is in the atom a fundamental quantity which increases by regular steps as we pass from one atom to the next. The quantity can only be the charge on the central positive nucleus.”

2.7 The Periodic Law. When the elements are arranged in the order of their atomic numbers, the anomalies of the Mendeleev classification according to atomic weights disappear. Potassium follows argon, nickel follows cobalt, and iodine follows tellurium, despite the fact that according to the atomic-weight classification they are in the reverse order. From the results of Moseley's investigations it is now recognized that the chemical and most of the physical properties depend on the number and arrangement of the extranuclear electrons, rather than on the atomic weight. His work also permits us to restate the periodic law in a manner that is more satisfactory than the one formulated by Mendeleev on the basis of atomic weights. This law may now be stated as follows: *The properties of the elements are periodic functions of their atomic numbers.*

The relationship among the elements indicated by their atomic numbers not only predicted that the number of total elements was limited but gave valuable information regarding those elements which were missing at that time. Since Moseley's measurements gave the atomic numbers of the missing elements, it was a simple matter to calculate where their X-ray spectral lines should fall in relation to the known elements. This was an important guide in the quest for the hitherto unknown elements and was also one means of identifying these elements in the process of the search. Among the elements revealed by X-ray analysis shortly after Moseley's experiments were hafnium, protactinium, and rhenium. The assignment of atomic numbers to successive elements also removed all doubt concerning the number rare earth metals. Up to this time there had been some confusion as to the number of these metals, since their chemical properties were so much alike.

✓ QUANTUM THEORY

Rutherford's model of the atom has been described as containing a small, yet heavy, positively charged nucleus with a number of light, negatively charged electrons revolving around it, both bodies being under the action of mutual electrical attraction. For many years it was customary to describe this model as being analogous to our sun's planetary system, in which the planets are held in position by gravitational and centrifugal forces. The analogy has been made even more striking by the fact that both electric and gravitational forces vary in inverse proportion to the square of the distance, and, in consequence, both lead to the same type of elliptic orbit.

There is one important difference between the forces operating in an atom's structure and the sun's planetary system. Within the atom the electrons revolving around the nucleus carry relatively large electric charges, and, according to the classical electromagnetic theory, such rotating electrons should continuously emit energy as radiation because of their motion. Moreover, if an electron were constantly emitting electromagnetic waves, it must also be losing kinetic energy as a result of the emission. If this were true, an electron would describe a spiral path of decreasing curvature until it eventually entered the nucleus. Furthermore, since the radius of curvature would be steadily decreasing for such a hypothetical electron, the radiation which is emitted should cover a continuous range of wavelengths varying from visible light to X rays. However, we know that such a spectrum is not produced. Electron orbits are relatively stable, and when atoms are excited by external means, the resulting atomic spectra consist of well-defined lines.

In order to endow Rutherford's model of the atom with stability, Niels Bohr,¹ in 1913, postulated that atomic phenomena must be subject to quantum laws rather than the laws of classical electromagnetic theory. To describe adequately Bohr's theory of atomic structure, it will be necessary, first, to give some brief consideration to the Planck theory of discontinuous energy changes, which provided the basis for the Bohr theory.

2.8 Origin of the Quantum Theory. The quantum theory had its origin in an effort to account for the radiation by black bodies. A *black body* is generally understood to be a body which absorbs all the light falling upon it and, accordingly, can reflect none. Physicists, on the other hand, use the term in a much broader sense; by their interpretation a perfect black body is one which at all temperatures absorbs all the radiation falling upon it, whether it be visible light, ultraviolet, or infrared radiation. Moreover the black body is an ideal radiator: the energy emitted per unit area at any temperature is equal to that absorbed. However, the nature of the radiation emitted by a black body depends on its temperature. The emitted radiation is not uniform but has a maximum value at a definite wavelength which is inversely proportional to the absolute temperature, and the total energy that is emitted varies as the fourth power of the temperature. A heated solid emits radiation through a whole range of wavelengths, and if the energy is plotted in the form of a graph against the wavelength, the curve shows a maximum. The classical theory predicted that most of the energy should be in the form of the shortest wavelengths (Fig. 2-6). Furthermore, according to the classical theory, the light emitted by a body should remain the same color, only its intensity altering with temperature. It is a well-known fact that a heated body changes through red and yellow to white as its

¹ N. Bohr, *Phil. Mag.*, **26**: 1 (1913).

temperature increases. To overcome the difficulties in explaining the black-body spectrum, Max Planck, in 1900, arrived at the revolutionary conclusion that radiation is emitted and absorbed discontinuously in integral multiples of a fundamental unit which he designated as a quantum, the energy of this unit being proportional to the frequency of light. This conclusion led to the development of the quantum theory.

2.9 Planck's Quantum Theory. A black body is one which will absorb completely incident radiation of any wavelength. The ideal black body does not reflect any energy, but it does radiate; in fact it is the most efficient possible emitter of radiation. For this reason such a body is sometimes called a *complete radiator*. Although no actual body is perfectly black, it is possible to postulate a condition where radiation is completely enclosed in a space surrounded by thick walls at a constant temperature. Thus we may imagine a cavity inside a solid body containing a small hole in one wall whereby the investigator may study the enclosed radiation without altering its character. The perforation in the wall must be sufficiently large so that light may be removed for analysis by means of a spectroscope, but it must be small enough so that the light which comes out will be a representative sample of what the light would have been if the hole had not been there.

The inside walls of the cavity are emitting as well as absorbing radiant energy, and the total energy of the radiation is proportional to the fourth power of the temperature. If we should attempt to increase the amount of light in the cavity by passing a beam of light through the hole, it would produce only a temporary change. The radiation would be absorbed in the walls of the enclosure and their temperature increased as a result, but as soon as the beam were removed, the temperature would revert to its original value, since it was postulated that the enclosure should be kept at a constant temperature; consequently the same amount of light, or radiation, would remain in the cavity. Figure 2-7 is a sketch of an enclosure of this description.

The light emerging through the hole has a distinctive spectrum, usually referred to as the *black-body spectrum*, and, in accordance with our original assumptions, it will be identical with the spectrum of the light inside the cavity. If the energy emitted is plotted against its frequency or wave-

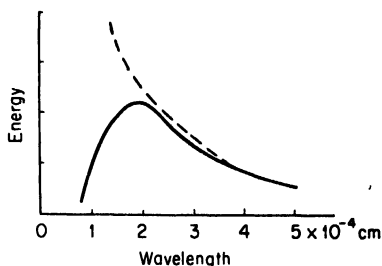


Fig. 2-6 Spectral distribution of energy of black-body radiation at 1500°K . The curve represents the observed distribution of energy among different wavelengths. The dotted line represents the distribution of energy as predicted by the classical theory.

82 Fundamental Concepts of Inorganic Chemistry

length, where $\nu = c/\lambda$, the curve shows a maximum, as indicated in Fig. 2-8. This graph shows that the energy emitted is greatest at the middle wavelengths in the spectrum and least at the highest and lowest frequencies. If curves are plotted for a series of temperatures, as given in Fig. 2-8, it is found that the maximum moves toward shorter wavelengths as the temperature rises.

Max Planck, in 1900, developed an empirical equation which satisfactorily represented the experimental data obtained for the energy distribution in the spectrum of a black body. However, he was unable to justify this equation by theoretical reasoning upon the basis of the classical electromagnetic wave theory. Furthermore the classical conceptions

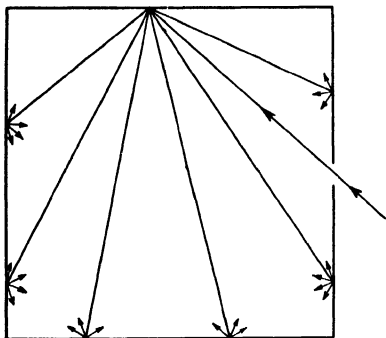


Fig. 2-7 A black-body enclosure with a small opening in one wall.

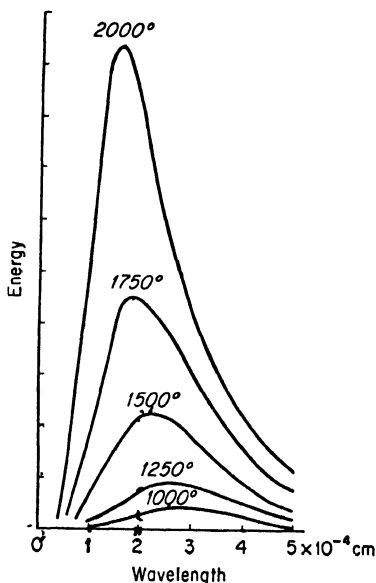


Fig. 2-8 Energy distribution for black-body radiation at different absolute temperatures.

of continuity completely broke down in an endeavor to explain the results of these experiments. Consequently Planck reached the conclusion that the laws of classical physics do not apply to energy transformations on an atomic scale. In order to explain the black-body spectrum, he postulated that all solid bodies, including the walls of the cavity, consisted of an enormous number of elementary oscillators, vibrating at all possible frequencies. These oscillators, which he called "resonators," were conceived by Planck to be small electrified particles in constant motion; later he identified them as vibrating electrons, but in 1900 the electronic concept of matter was not well established. According to this theory there must be oscillators in all radiating bodies for any possible range of frequencies. Moreover the energy of any one oscillator of frequency ν could

assume only such values as were integral multiples of a unit e , which in turn was proportional to the frequency ν , the proportionality factor being the universal constant h . This postulate was expressed in the equation

$$e = h\nu$$

where h is usually called *Planck's constant*. In other words, the energy of any one oscillator was not permitted to take any arbitrary value but was proportional to some integral multiple of the frequency of the oscillator. This was a radical break with the classical theory, which postulated that all such oscillators must have the same energy, no matter what their frequency, and that, although the amount of energy for any oscillator might vary, the variation must be a continuous one, up or down, through the energy scale.

In explaining the experimental data for black-body radiation, as shown in Fig. 2·8, at low temperatures, only those oscillators with low natural frequencies are excited; therefore the radiating body can emit only light of low frequency. Since more oscillators have high frequencies, more radiation takes place as the temperature is raised. Accordingly the energy of the black body is not continuously variable but is emitted in small packets, and the number of packets is increased with temperature.

2·10 Photoelectric Effect. From the study of X-ray spectra (Sec. 2·5) we have learned that, when particles of matter with suitable velocities strike a metal surface, the energies of the particles can be absorbed by the surface and then emitted in the form of radiation. The reverse transformation is also possible. A beam of light of suitable frequency falling upon a metal surface will cause the emission of electrons. This phenomenon is called the *photoelectric effect* and provides the basis for the photoelectric cells used for commercial purposes. Although this effect was first observed by Heinrich Hertz in 1887, credit is usually given to Hallwachs, who, in 1888, announced that a freshly polished zinc plate would lose its charge when charged negatively and illuminated by ultra-violet light but would not lose its charge when charged positively.

The spectral sensitivity of a surface depends upon the nature of the metal used. Those metals which are the best conductors of electricity, and presumably have the largest number of free electrons, are not the ones that show the greatest photoelectric action. There seems to be some relation between chemical reactivity and photoelectric effect, since those metals which are most active, photoelectrically, are those with few electrons in their outermost shells, particularly those which have only one, such as sodium, potassium, etc. Thus the feeble light of a candle falling upon the surface of the alkali metals is sufficient to cause the emission of electrons. Those metals with two electrons in their outermost shell, e.g., magnesium and zinc, act in a similar manner when sub-

84 Fundamental Concepts of Inorganic Chemistry

jected to radiation of greater frequency, such as ultraviolet light. Other metals are also slightly active, although X rays and gamma rays are sufficiently powerful to cause the emission of electrons from all forms of matter. These facts lead us to conclude that the energy of the electron which is emitted comes from the light beam, and not from the atom itself.

Electrons emitted by the action of radiant energy are called *photoelectrons*. The maximum velocity attained by these electrons varies directly with the frequency but is independent of the intensity of the radiation that liberates them. A very weak beam of light of high frequency can liberate electrons that travel with a high velocity, whereas a low-frequency ray of light, regardless of intensity, may liberate only low-speed electrons. An increase in intensity merely serves to increase the number of photoelectrons.

2.11 Einstein's Concept of Light Quanta. In 1905 Einstein extended the quantum theory, as proposed by Planck, by suggesting that radiation is not only absorbed and emitted in quanta but that it is propagated through space in definite quanta called *photons*. The energy of each individual light quantum, or photon, is given by the expression $h\nu$, where h is Planck's constant and ν is the frequency of the light. Einstein also suggested that the photoelectric process could be explained by assuming that the energy of a photon, $h\nu$, was absorbed by an electron and converted into kinetic energy, whereby the electron was enabled to escape from the surface of a metal. The equation he developed for the process was

$$\frac{1}{2}mv^2 = h\nu - W$$

in which the expression $\frac{1}{2}mv^2$ denotes the kinetic energy of the emitted electrons, $h\nu$ is the energy of a photon, and W is the work required to remove the electron from the metal surface. Thus the kinetic energy of the emitted electron will always be less than that of the incident photon because of the energy necessary to release the electron from the surface. The equation also explains why the number of emitted electrons is proportional to the intensity of the light.

The foregoing mathematical expression is known as *Einstein's photoelectric equation*. The validity of the equation has been justified by numerous experiments, and it also has served as a basis for determining the value of Planck's constant h . The interpretation of the equation has been simplified by the modern theory of metals. A metallic conductor is believed to be made up of a lattice of positive ions, permeated by loose electrons which are in random motion. An electron may come to the surface of a metal, but it cannot escape because of a potential difference between the metal and the surrounding space. The photo-

electric effect is produced by light of sufficiently short wavelength falling upon a metal surface and imparting to some of the electrons enough energy to permit them to penetrate the potential barrier. However, unless the frequency of the incident radiation exceeds a minimum value, so that $h\nu$ is greater than W , there can be no photoelectric emission of electrons. It is an all-or-none process in which the electron either acquires all the energy of the photon and escapes from the surface or accepts none of it and remains within the potential barrier of the metal.

2.12 The Compton Effect. Additional evidence of the corpuscular nature of electromagnetic radiation (light) is furnished by the change in wavelength of X rays when they are scattered upon impact with atoms or molecules. This phenomenon was observed by A. H. Compton in 1923 and is therefore usually referred to as the *Compton effect*. It differs from the photoelectric effect in respect to the amount of energy absorbed by an electron within a surface. The photoelectric effect involves the complete absorption of a quantum, whereas in the Compton effect only a portion of a quantum is imparted to an electron.

According to the classical electromagnetic wave theory, monochromatic light falling upon matter should be scattered without change in frequency. However, when Compton permitted monochromatic X rays to impinge upon matter of low atomic weight, he observed that secondary X rays of slightly longer wavelength than those of the impinging beam were produced. In other words, when a photon collides with an electron, it may leave with a lower frequency, and the electron thereby acquires a greater velocity. In the collision the energy of the photon is reduced, and the energy of the electron is increased.

The Compton effect may be explained as resulting from an impact between two bodies, the photon and the electron, which is, of course, additional proof of the corpuscular nature of light. This impact is elastic, and both kinetic energy and momentum are conserved. After the encounter each body has a different energy and a different momentum from the values it had before the contact, but the sum of the energies and the sum of the momenta are unchanged. Compton assumed that the same principles for conservation of energy and for change in momentum apply to the impact between a photon and an electron as apply to the collision of any other two moving bodies.

The energy of a quantum is equivalent to $h\nu$, and if the quantum is considered as a particle, which we shall call a photon, it possesses momentum equivalent to $h\nu/c$, where c is the velocity of light. When the photon collides with an electron, the electron gains momentum and the photon is deflected with a loss of momentum. Since h and c are constants and do not change, the energy transformation is manifested as a lowering of frequency (wavelength is increased) for the photon as a result of the collision.

86 Fundamental Concepts of Inorganic Chemistry

Following the encounter between the two bodies, the photon moves in one direction at an angle θ (Fig. 2-9) with momentum equal to $h\nu\theta/c$, and the electron recoils in another direction at an angle ϕ with momentum equal to $mv\sqrt{1-\beta^2}$, where β is the ratio of the velocity of the electron to the velocity of light. It can be shown mathematically that

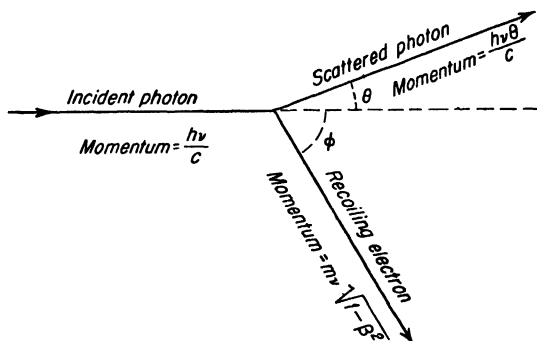


Fig. 2-9 Collision between a photon and an electron; the Compton effect.

the change in wavelength, where $\lambda = c/\nu$, of the photon is given in the equation

$$\Delta\lambda = \frac{h}{mc} (1 - \cos \phi)$$

where m is the rest mass of the electron. Inasmuch as h , m , and c are all constants, the equation can be simplified to

$$\Delta\lambda = 0.024(1 - \cos \phi)$$

The evidence of the Compton effect is of great significance. It indicates that X rays normally thought of as radiation can also be treated as particles, using classical laws.

✓ ATOMIC SPECTRA

When elements or their compounds are heated in a flame or by means of an electric arc, they emit energy in the form of light. Analysis of this light with the aid of a spectroscopy yields a discontinuous spectrum. A spectroscopy is an optical instrument which is nothing more than a refinement of a prism and is used for dispersing complex radiation into a spectrum for visual observations; or, more simply, it is a device for separating light into its components, each of which has a different wavelength. A discontinuous spectrum may appear in the form of a series of lines, or the lines may be so closely grouped that they appear as bands. The first is known as the *line spectrum* and is typical for particular atoms,

and the lines, corresponding to definite wavelengths, are spaced according to certain exact physical laws; the second is known as the *band spectrum* and is characteristic of molecules or groups of atoms. The line spectrum is also called the *atomic spectrum*, since it originates in the atom of the element, and each element has a different atomic spectrum.

Long before the theory of the nuclear atom came into existence, it was known that the line spectrum is a unique property of an element and that each element emits a spectrum which is characteristic of it and different from the spectrum of every other element. The very fact that line spectra existed led to the conclusion that the structure of the atom must be quite complex to give rise to such spectra. Moreover the discovery of the existence of certain relationships among the lines of any particular element laid the foundation for the present view of atomic structure. In order to explain the spectra of the elements, Niels Bohr, in 1913, proposed the hypothesis that electrons exist in definite energy levels, without emitting or absorbing radiation, but that, when an electron moves from one level to another, monochromatic radiation is emitted or absorbed. Not only does the Bohr model of the atom explain atomic spectra, but, conversely, it is due to a knowledge of spectral lines and their relationships that has permitted the construction of the atomic model with its arrangement of external electrons. Hence a brief survey of atomic spectra is the best introduction to the discussion of Bohr's atomic model.

2.13 Excitation of Spectra. The spectra which are emitted or absorbed by different types of bodies when excited by various means may be classified in numerous ways. Since we are primarily interested in the evolution of theories regarding the structure of the atom from observations of body radiations, we shall concern ourselves with only a minimum consideration of such phenomena. We have discussed the use of X-ray spectra in the determination of atomic numbers in Sec. 2.5. Our present interest will be devoted largely to an examination of spectra emitted by the atom which are usually termed atomic, or line, spectra.

The electrons distributed about an atom are believed to be grouped in energy shells, and there is an increase by one electron for a corresponding increase in the atomic number of the element until a shell is completed, whereupon another shell is started. For the higher atomic numbers incomplete shells may be formed which remain unfilled even after another shell has been started.

When energy is supplied to an atom, the outermost electrons are those most likely to absorb the energy, at least momentarily. The energy acquired by an electron causes it to move an added distance from the nucleus. Both the energy absorbed and the distance moved are discontinuous, occurring in discrete quantities, steps, or levels. An electron which has been removed from a given energy level within the influence

88 Fundamental Concepts of Inorganic Chemistry

of an atomic nucleus may fall back to its original level, either in one step or in a series of steps, and in doing so will emit energy in the form of light. A more detailed explanation of this phenomenon is given in the Bohr theory of atomic structure within Secs. 2.16 to 2.18. We are at present interested in the fact that, as an electron returns to its original level, the frequency of the light emitted is proportional to the change in energy experienced by the electron. The discrete amounts of energy which may be emitted produce a limited number of frequencies, and a measurement of the frequencies in the form of lines upon a spectral scale constitutes a method of identification for the particular atom.

It will be recalled from Fig. 2.4 that a photograph of the X-ray spectra of a series of elements, on which the spectrum of each element is shown separately, indicates that elements of successive atomic numbers when arranged serially have line spectra which are similar except that there is an orderly shifting of wavelengths with increasing atomic numbers. No such uniform arrangement of similar, regularly displaced lines appears in the optical spectra of the different elements. The atomic spectrum of one element differs greatly from the spectrum of another element, even though their atomic numbers are in sequence. Not only is there a wide difference in the arrangement of the lines which make up two such spectra, but it is impossible to detect any correlation between the wavelengths of the individual lines of the spectra.

Another feature of atomic spectra is the fact that the spectrum of a given element depends a great deal upon its mode of excitation. If we confine the discussion to the amounts of energy supplied to an atom in the form of heat, several possibilities may occur. Since atomic spectra arise from electrons being excited to levels above their ground states, a minimum amount of energy must be supplied to produce the excitation. If the energy is insufficient to move an electron from its normal level, no spectra are emitted and the added energy may be absorbed by the atom in the form of increased kinetic energy.

If the energy accepted by an atom is sufficient to move an electron through the distance of one energy level, it will emit only one wavelength of light upon returning to the unexcited, or "ground," state. This amount of energy varies for atoms of different elements; however, the spectral line so produced is called the *persistent line* since it is the line most easily detected for a low concentration of the element.

When sufficient energy is supplied to an atomic system to move electrons several energy levels away from their ground states, they may return in a series of moves, emitting different wavelengths of light for each step. Therefore, as more energy is added to the atoms of an element, more spectral lines may appear in the spectrum of the element. Furthermore an electron which is far removed from the nucleus may return to its ground state without emitting the persistent line of element.

Another minimum energy acceptance of an atomic system is that which is designated as the *first ionization potential* of an atom. This is the amount of energy which must be supplied to an electron to remove it completely from the electrostatic field of the nucleus of the particular atom. The wavelength of light emitted by an atom with an electron removed is termed the *spark resonance* and appears as a persistent line. More lines may be emitted by the ion as it accepts energy of increased magnitude, up to a point where a second electron is lost, which loss is described as the *second ionization potential*. The foregoing operation may be repeated as long as electrons remain to be removed from the atom.

2.14 ✓ **The Hydrogen Spectrum.** The atomic spectra of most of the elements contain so many lines that any attempt to correlate, interpret,

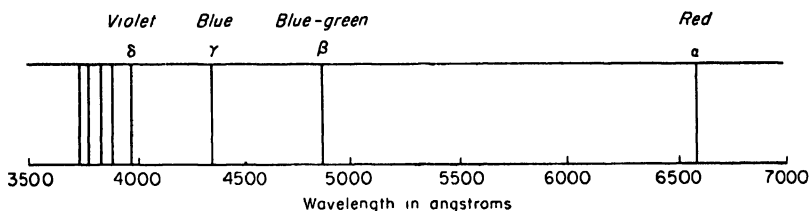


Fig. 2-10 The Balmer-series spectrum of hydrogen. These lines which are in the visible light range result from changes in the energy content of the atom's electron.

or classify them is almost a hopeless task. The spectrum of the hydrogen atom is comparatively simple, or at least it is the simplest of the various atomic line spectra; consequently most of the applications of spectral data to the interpretation of atomic structure have been made from the spectrum of this element. The four most prominent lines which appear in its visible region were first studied in the spectrum of the sun, and because of their regular spacing these lines have been designated as $H\alpha$, $H\beta$, $H\gamma$, and $H\delta$. The four bright lines emitted by luminous hydrogen appear in the red, blue-green, blue, and violet regions, respectively, but if a camera is substituted for the eyepiece of the spectroscope, many other lines are observed upon a photograph of the spectrum. The relative positions of a few of these lines appear in Fig. 2-10.

Within the region of visible light and including the range of the longest ultraviolet wavelengths there is a group of lines called the *Balmer series* (Fig. 2-10), named after J. J. Balmer, who discovered the relations of these lines to one another. In 1885 Balmer found that the wavelengths of the hydrogen lines beginning with $H\alpha$ could be expressed by means of the formula

$$\lambda = k \frac{n^2}{n^2 - 4}$$

where λ is the wavelength in angstroms, k is a constant, and n is an

90 Fundamental Concepts of Inorganic Chemistry

integer equal to 3, 4, 5, 6, etc., for the $H\alpha$, $H\beta$, $H\gamma$, $H\delta$ lines, respectively. The agreement between observed wavelengths and those calculated from the above formula is shown in Table 2.1.

TABLE 2.1 WAVELENGTHS, ANGSTROMS, OF LINES IN THE BALMER SERIES OF HYDROGEN

Line	n	Observed by Balmer	Calculated by Balmer
$H\alpha$	3	6,562.10	6,562.08
$H\beta$	4	4,860.70	4,860.80
$H\gamma$	5	4,340.10	4,341.00
$H\delta$	6	4,101.30	4,101.20

A spectral line of hydrogen might be designated by its frequency as well as its wavelength, but this would lead to inordinately large numbers. A new term, related to frequency and wavelength, has been invented for describing a spectral line which is called the *wave number*. The wave number is the reciprocal of wave length and is also the number of wave lengths per centimeter. We shall symbolize this term as $\bar{\nu}$. Since the relationship between wave number and wavelength is

$$\bar{\nu} = \frac{1}{\lambda}.$$

the Balmer formula may be more conveniently expressed as

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

where R is an important constant known as the Rydberg constant and n is a whole number equal to, or greater than, 3.

It is pertinent at this point in our discussion to call attention to the fact that the same formula for the Balmer series, as given above, was later derived by Niels Bohr upon the basis of theoretical calculations involving his model of the hydrogen atom.

Balmer's discovery provided impetus to investigations within the field of spectral emission, and, after the beginning of the twentieth century, other series of lines were discovered in the hydrogen spectrum. Of these we shall mention only two: the Lyman series in the ultraviolet, and the Paschen series in the infrared. The locations of these series in relation to the Balmer series, on the wavelength scale, are given in Fig. 2.11. Formulas for these two series are as follows:

$$\text{Lyman series: } \bar{\nu} = R \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \text{ etc.}$$

$$\text{Paschen series: } \bar{\nu} = R \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \text{ etc.}$$

For the spectra of atomic hydrogen the wave number of any spectral line within any of its spectral series may be represented by the general equation

$$\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where n_1 is 1, 2, or 3 for the Lyman, Balmer, and Paschen series, respectively, and n_2 is a whole number greater than n_1 by at least 1. R is the Rydberg constant, which has been determined as $109,677.8 \text{ cm}^{-1}$. However, this general equation for the atomic spectrum of hydrogen is only

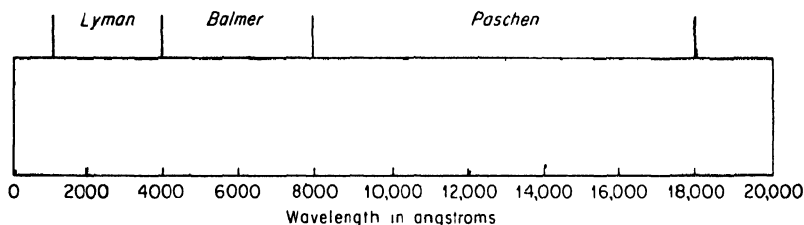


Fig. 2.11 The relative locations of the Lyman, Balmer, and Paschen series of spectral lines for atomic hydrogen on a wavelength scale.

a special form of a more general equation representing the *Ritz combination principle*.

ψ 2.15 Ritz Combination Principle. Upon examining the formulas for the Balmer, Lyman, and Paschen series it can be seen that they consist of two terms, one of which is constant for a given series and the other variable from term to term within the series. A general interrelation between the spectral series of a given atom or ion was postulated by W. Ritz in 1908, who stated that the wave number of any spectral line may be represented as a combination of two terms, one of which is constant and the other variable throughout each spectral series. The general formula embodying Ritz's combination principle may be written as

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

where x and y are integers for hydrogen, but not necessarily so for other atoms. There are only a few elements or ions, such as hydrogen, singly

92 Fundamental Concepts of Inorganic Chemistry

ionized helium, and doubly ionized lithium, whose spectra may be represented by the Balmer type of formula given in Sec. 2-14. For heavier elements it is possible to separate their more complicated spectra into series and to express the wave number of each line as a difference of two terms, as indicated in the foregoing combination principle. The Ritz principle applies throughout the entire range of possible spectroscopic investigation, from X rays to the infrared, and has served as a guide in correlating spectral studies with the theories of atomic structure.

✓BOHR'S MODEL OF THE ATOM

In 1913 Niels Bohr, a Danish physicist, after working for a short time with Ernest Rutherford, advanced his own theory as to the structure of the atom. At this particular time physics, as regards radiation problems, was in a chaotic state. There existed four branches of knowledge, each apparently well founded in itself, among which there was no connecting link; in fact they were in many respects contradictory with each other. These four branches were the classical electromagnetic theory of light, the empirical knowledge of atomic spectra, Planck's quantum theory of heat radiation, and Rutherford's model of the nuclear atom. The Bohr theory of the atom succeeded to some extent in correlating the last three areas of knowledge, but, in respect to the classical electromagnetic theory, Bohr agreed with Planck's conclusion that the classical laws of physics do not apply to atomic phenomena.

2-16 Fundamental Assumptions. Bohr adopted the Rutherford nuclear model of the atom with certain reservations and additional assumptions. It will be recalled that Rutherford postulated that the atom consists of a positively charged nucleus, containing practically all the mass, surrounded by a planetary system of electrons whose number is equal to the nuclear charge. Furthermore Rutherford found it necessary to assume that the electrons were in rapid motion about the nucleus, so that the attractive force of the nucleus was exactly counterbalanced by the outward centrifugal force produced by the electron's motion. We have already pointed out that such an atom would be extremely unstable, since according to the electromagnetic theory an electron in motion would emit radiation, thereby losing kinetic energy, which should result in a constantly decreasing curvature of its path until the electron would eventually fall into the nucleus. To overcome the objections to the Rutherford model, and also to explain the spectrum of atomic hydrogen, Bohr made the revolutionary suggestion that an electron could rotate in a stable orbit, or stationary state with respect to the nucleus, without emitting or absorbing energy. This suggestion with his other assumptions are contained in the following postulates:

1. An atom has a number of stable orbits, or "stationary states," in which an electron can reside without the emission of radiant energy.

2. An electron may pass from one of its designated nonradiating orbits to another of lower energy; however, in doing so, radiation is emitted whose energy equals the energy difference between the initial and final states and whose frequency ν is given by the relation

$$h\nu = E_2 - E_1$$

where h is Planck's constant and E_2 and E_1 are the initial and final energies.

3. If an electron moves in a circular orbit, its motion is governed by the ordinary laws of mechanics and electrostatics provided its angular momentum is an integral multiple of $h/2\pi$.

2.17 Bohr's Theory of the Hydrogen Atom. Bohr pictured the hydrogen atom as a system consisting of a single electron with a charge designated as e , rotating in a *circular* orbit of radius r about a nucleus of charge Ze . According to Coulomb's law the electrostatic force of attraction F_e between the charges may be evaluated mathematically as

$$F_e = \frac{Ze^2}{r^2} \quad (2.1)$$

By definition the magnitude of the centrifugal force F_c for an electron of mass m , with a velocity in its orbit of v , and with an orbital radius of r , is given as

$$F_c = \frac{mv^2}{r} \quad (2.2)$$

In order that the electron's orbit may remain stable, it is necessary to assume that the two forces, electrostatic and centrifugal, are equal and opposed to each other. From this assumption may be deduced the following mathematical relationship,

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad (2.3)$$

and, upon solving for v , we obtain

$$v = \sqrt{\frac{Ze^2}{mr}} \quad (2.4)$$

The angular momentum of the electron is defined as the product of the velocity of the electron in its orbit, its mass, and the radius of its orbit. This product is symbolized as mvr . One of the original assumptions of the Bohr theory postulated that an electron is restricted to those orbits whose angular momenta are whole multiples of $h/2\pi$. Therefore, accord-

94 Fundamental Concepts of Inorganic Chemistry

ing to this quantum restriction, angular momentum may be described as

$$mvr = \frac{nh}{2\pi} \quad (2.5)$$

where n represents an integer. If this equation is also solved for v , the result is

$$v = \frac{nh}{2\pi mr} \quad (2.6)$$

Equations (2.4) and (2.6) may be equated since they are equal to each other,

$$\sqrt{\frac{Ze^2}{mr}} = \frac{nh}{2\pi mr} \quad (2.7)$$

and, upon solving for r , we obtain

$$r = \frac{n^2 h^2}{4\pi^2 m Ze^2} \quad (2.8)$$

Consequently the radius r_0 of the smallest orbit for the hydrogen atom is

$$r_0 = \frac{h^2}{4\pi^2 m e^2} \quad (2.9)$$

By definition the kinetic energy of any body in motion is equal to the product of one-half the mass of the body by the square of its velocity. Hence the kinetic energy of an electron is equal to $\frac{1}{2}mv^2$. The total energy E of the electron is the sum of its kinetic and potential energies. If the potential energy of an electron is taken as zero when it is at an infinite distance from the nucleus, the value at a distance r is given by $-Ze^2/r$. This value may be obtained by integrating Eq. (2.1) between the limits of r and infinity. The negative sign indicates work must be performed on the electron to transfer it to infinity. Therefore the total energy of the electron is

$$E = \frac{mv^2}{2} - \frac{Ze^2}{r} \quad (2.10)$$

From Eq. (2.3) we may obtain

$$\frac{mv^2}{2} = \frac{Ze^2}{2r} \quad (2.11)$$

and upon combining Eqs. (2.11) and (2.10) the following expression may be derived:

$$E = - \frac{Ze^2}{2r} \quad (2.12)$$

Now, if we substitute the value of r from Eq. (2-8) into Eq. (2-12), the total energy of the electron may be stated as

$$E_n = - \frac{2\pi^2 Z^2 e^4 m}{n^2 h^2} \quad (2-13)$$

where E_n is the total energy of the electron in the orbit designated by the quantum number n .

✓ **2-18 Origin of Spectral Lines.** In the preceding section we have symbolized the distance of an electron from the nucleus, and its total energy when residing in the orbit n of the hydrogen atom, where n is an integer. We are now enabled to consider the process by which the various spectral series are produced. According to Bohr's original theory the energy levels of the hydrogen atom correspond to a series of circular electron orbits, and the spectral series are produced by the passage of an electron from one level to another. In our present discussion the word *orbit* is used interchangeably with the term *energy level*. As described by Bohr, energy is radiated when an electron moves from an orbit of a quantum number of n_2 to an orbit of quantum number n_1 , where n_1 is the inner orbit. Energy is absorbed if the electron moves in an opposite direction, i.e., from the orbit designated as n_1 to the one indicated as n_2 . Moreover, since the total energy of an electron is a specific, yet different, quantity for each of the two orbits n_1 and n_2 , it is apparent that a definite amount of energy is radiated or absorbed as the electron moves from one quantum level to another. The energy E which is emitted may be represented as a difference in energy of the two electronic states and can be indicated by the equation

$$E = E_1 - E_2 = h\nu$$

where E_2 represents the total energy of the electron in the outer energy level and E_1 the total energy in the inner energy level. This difference may be equated to $h\nu$, where h is Planck's constant and ν is the frequency of the radiation which is emitted.

According to our notation the orbit designated as n_1 in the hydrogen atom is called the normal orbit, or ground state, and represents the stationary state of the unexcited atom. Energy may be imparted, in discrete quantities, to an electron by thermal agitation or by collision with another particle, resulting in the removal of the electron from its normal orbit to a higher quantum state. In the new level the electron possesses more energy and, having left its normal orbit, is less stable than before. Unless the electron receives additional packets of energy to enable it to escape from the nuclear electrostatic field, it will eventually fall toward the nucleus until it reaches either the normal orbit or some intermediate level. In the process of this transition the total energy of the electron

96 Fundamental Concepts of Inorganic Chemistry

(as well as the atom) is reduced, and the energy so lost is radiated as a photon, or photons, of frequency ν , as indicated in Eq. (2·14).

Spectral lines are produced by the radiation of photons, and the position of the lines on the spectral scale is determined by the frequency, or frequencies, of the photons emitted. Transitions to the innermost level, which we have designated as n_1 , or $n = 1$, from orbits n_2 , n_3 , n_4 , etc. ($n = 2, 3, 4$, etc.) give rise to the first, second, third, etc., lines of the Lyman series in the ultraviolet. Transitions from the outermost energy

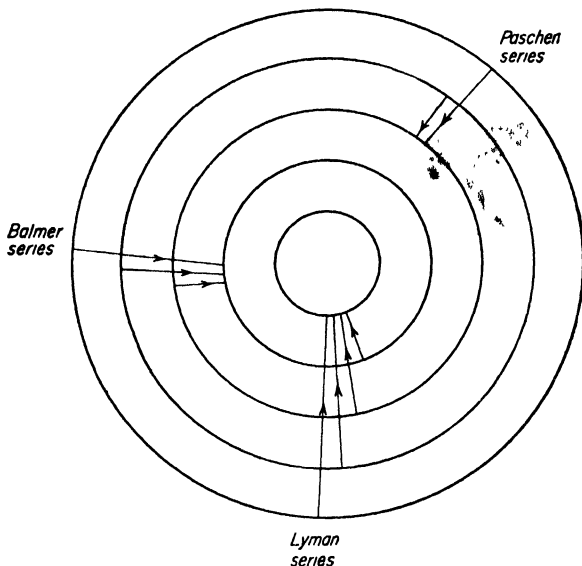


Fig. 2·12 The origin of spectral lines of the hydrogen spectrum.

levels give rise to spectral lines of higher frequencies. Shifts of electrons to the n_2 level ($n = 2$), or second quantum level, from outer levels give Balmer lines in the visible-light region. Similar transitions from higher orbits to the third orbit ($n = 3$) produce the Paschen series in the infrared. Other series of lines have been discovered for similar shifts in the far-infrared region. A sketch indicating the transitions which produce three of these spectral series is given in Fig. 2·12. Another method of portraying the origin of the spectral series in the spectrum of atomic hydrogen is shown in Fig. 2·13. In the latter diagram the arrows represent the transitions of an electron from outermost to inner energy levels, and consequently, the origins of the various spectral lines.

Bohr's original theory was remarkably successful in accounting for the main features of the hydrogen spectrum. There is a direct relation

between the general equation for the spectral series and the one for the total energy of an electron in a hydrogen atom. One of Bohr's original assumptions (Sec. 2.16) postulated that, when an electron passes from one orbit to another of lower energy, radiation (a photon) is emitted whose energy equals the energy difference between the initial and final

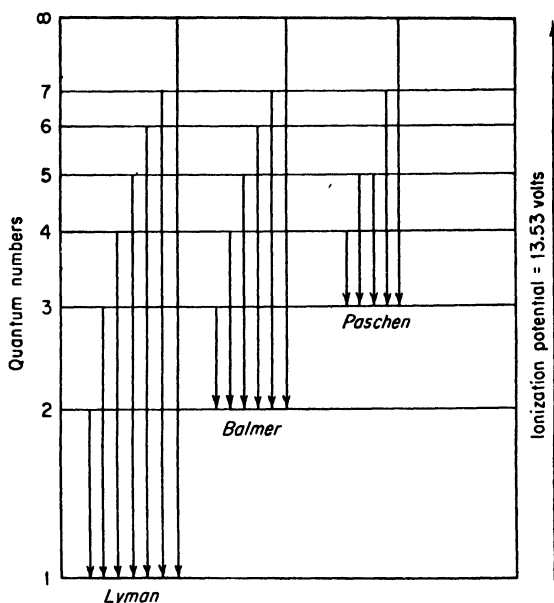


Fig. 2.13 Origin of emission spectra of atomic hydrogen.

states. If we indicate the energy of the higher level as En_2 and that of the lower as En_1 , then the difference may be expressed as

$$h\nu = En_2 - En_1 \quad (2.14)$$

From Eq. (2.13) we have designated the total energy of an electron in an orbit n as En ; therefore the difference between the energies of an electron in the two orbits n_2 and n_1 may be indicated as

$$En_2 - En_1 = \frac{2\pi^2 Z^2 e^4 m}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2.15)$$

and if we substitute the term wave number for frequency,

$$\bar{\nu} = \frac{\nu}{c} \quad (2.16)$$

98 Fundamental Concepts of Inorganic Chemistry

where c is the velocity of light, we may then combine Eqs. (2.13) to (2.16) to give

$$\bar{\nu} = \frac{2\pi^2 Z^2 e^4 m}{h^3 c} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2.17)$$

All the terms in the fraction $2\pi^2 Z^2 e^4 m / h^3 c$ are constant; the number Z indicates that the number of the positive charge on the nucleus of atomic hydrogen is unity, and if we evaluate the fraction from the constant terms, the following value is obtained,

$$\frac{2\pi^2 1^2 e^4 m}{h^3 c} = 109,700 \text{ cm}^{-1} = R$$

where R is the Rydberg constant. Moreover, when we substitute R in Eq. (2.17), the relation becomes

$$\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2.18)$$

Equation (2.18) is identical with the general equation for the wave number of any spectral line within any of the spectral series of the hydrogen atom as given in Sec. 2.14. Not only did the identity of these two equations establish a foundation for the Bohr theory in terms of experimental measurements of spectral emissions, but the evaluation of the Rydberg constant gave, for the first time, a correlation between four fundamental physical constants, namely, the mass of the electron, m , the charge of the electron, e , the velocity of light, c , and Planck's constant h .

2.19 Limitations of the Bohr Theory. Bohr's model was very successful in accounting for the main features of the hydrogen spectrum, and also for the spectrum of singly ionized helium, which likewise has only one electron. However, it failed to predict the energy states of more complicated atoms. Some of the deductions from the theory were found not to be in agreement with the observed facts. Thus, when calculations are made of the energy required to remove an electron from any atom or ion, other than the hydrogen atom and the singly charged helium ion, the results definitely disagree with experimental data.

It is difficult to calculate the effect of other electrons upon the energy state of any one particular electron. Furthermore the pictorial concept of electrons jumping from one orbit to another is not justified because of the uncertainty of their positions and velocities. We now believe that values for the position and velocity of an electron cannot be evaluated simultaneously. Likewise, the practice of picturing an atom as consisting of a nucleus with a number of electrons moving around it, in fixed orbits oriented in space, is inaccurate because of the same uncertainty principle. At present we can only conclude that words are inadequate

and incapable of describing processes taking place within atoms. On the other hand mathematics does not suffer from the limitations of language, and the tendency is, more and more, to describe atomic processes in mathematical terms.

QUANTUM NUMBERS

Bohr's planetary model of the atom has been largely abandoned with the development of the theory of quantum mechanics. This new approach to the problem of atomic structure undertakes, not to calculate the path of an electron in its orbit, but rather to determine the probability of finding it in some particular region of space about the nucleus. The theory of quantum mechanics seems to be in complete agreement with the experimental information about the structure of atoms and, in this respect, is far superior to the Bohr concepts. We shall discuss the wave-mechanical atom in more detail in Secs. 2-27 to 2-29, but the Bohr theory with its visual pictures of the atom is not easily discarded. In an elementary discussion of atomic structure, such as we are attempting in this book, it is quite unsatisfactory to bring in the mathematical symbolism of wave mechanics, much of which is obscure to the student, in place of the atomic diagrams customarily used in explaining atomic structure according to the Bohr theory, regardless of how inadequate, incorrect, or incomplete the latter may be. Although the Bohr planetary model cannot accurately predict energy changes within complex atoms, it is still of great value in explaining qualitatively many of the chemical and physical properties of atoms with several electrons. Moreover, because of its great convenience in picturing atomic processes, even though the pictures may be somewhat inaccurate, we shall continue to use, as far as possible, the language and many of the ideas of the Bohr theory.

In the presentation of Bohr's theory of the hydrogen atom in Sec. 2-17 it was postulated that the electron orbits were circular. Also, according to our earlier discussion, the concepts of an electron orbit and an energy level were synonymous; however, later modifications of the Bohr theory have altered the meanings of these two terms. One of the original assumptions of the Bohr theory was to the effect that, if an electron moves in a circular orbit, its angular momentum is an integral multiple of $h/2\pi$. This integer is designated as n , which is a quantum number representing any particular energy level in which an electron might reside. The extension of the theory to include elliptic orbits made it necessary to introduce a second set of quantum numbers, and, in explaining the hydrogen spectrum according to the concepts of wave mechanics, other quantum numbers are necessary. In fact, to provide a complete

100 Fundamental Concepts of Inorganic Chemistry

description of an electron in an atom, four quantum numbers are needed. Moreover these quantum numbers describe the whole atomic state rather than particular orbits.

✓ **2-20 The Principal Quantum Number.** This number, designated as n , is identical with Bohr's integers and was introduced by him to account for the restricted nature of an atom's energy levels. The number also denotes the major axis of the orbit of the particular electron. On the basis of the Bohr theory it can be indicated mathematically in the equation

$$mvr = \frac{n\hbar}{2\pi}$$

where mvr signifies the angular velocity of the electron and $\hbar$ is Planck's constant.

The value of n for circular orbits indicates roughly the binding force and distance between the nucleus and the electron; hence this quantum number represents the *size of the electron orbit*. For the first energy level $n = 1$; for the second energy level $n = 2$; etc. The first energy level is the one nearest the nucleus. Formerly energy levels were described as electron shells, and, in the older notation, the innermost shell was indicated as the *K* shell and the succeeding outer shells were assigned the letters *L*, *M*, *N*, *O*, *P*, and *Q*.

2-21 The Azimuthal Quantum Number. This quantum number, designated as l , may also be described as the *second*, the *subsidiary*, the *lesser*, or the *orbital* quantum number. It denotes the angular momentum of the electron in its motion around the nucleus and is indicated mathematically in the equation

$$mvr = \frac{\hbar}{2\pi} \sqrt{l(l+1)}$$

In an attempt to account for the splitting of the lines in the optical spectrum of hydrogen into groups of finer lines, as observed by means of spectroscopes of high resolving power, Sommerfeld modified the Bohr atom by adding elliptical orbits. This refinement was also needed to explain the unusually low values for the energy levels of the alkali-metal spectra. According to this modification the electrons in any particular energy levels could have either a circular path or a variety of elliptical paths about the nucleus. Figure 2-14 illustrates the four possible Bohr-Sommerfeld orbits corresponding to a principal quantum number of 4. Sommerfeld postulated that the electron moves in an elliptical orbit with two degrees of freedom. The position of the electron in its orbit is determined by the radial distance from the focus (the nucleus is situated in this focus) and by the angle (azimuthal angle) between the variable

radius and the major axis of the ellipse. Figure 2-15 is a sketch of an orbit of this description. From this diagram, and from the experimental evidence of the alkali-metal spectra, it is apparent that an outer electron may penetrate the inner core of electrons and thereby experience a more powerful attraction from the high nuclear charge.

(Since the azimuthal quantum number indicates the ellipticity of the path of an electron, we may say that it describes the *shape of the electron's orbit*. The energies of elliptical orbits vary slightly for sublevels in a principal energy level. However, there is a limit to the number of different orbits an electron may assume in any main energy level. These

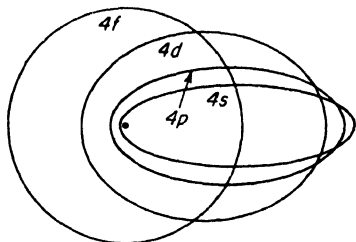


Fig. 2-14 The Bohr-Sommerfeld orbits, where $n = 4$.

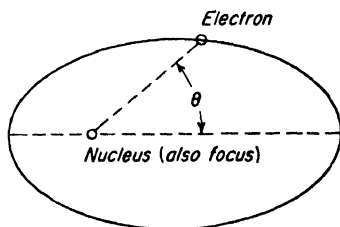


Fig. 2-15 The azimuthal angle, designated as θ .

possible paths are frequently referred to as *sublevels*, or in the older notation as *subshells*. If the principal quantum number is n , then the number of types of orbits (orbitals is a better word), or subshells, will equal n . Thus, where $n = 4$, the possible orbitals, or subshells, are four. Furthermore the quantum number l can have only a limited number of values in a neutral atom. These values range from zero as a minimum to $n - 1$ for a maximum. Electrons with $l = 0, 1, 2$, and 3 are called *s, p, d*, and *f* electrons. (These letters designate old spectral terms: *sharp, principal, diffuse, and fundamental*.) Although larger l values are possible, these four energy sublevels (orbitals) are all that are necessary to describe the electrons of neutral atoms. For $l = 0$ the angular momentum is zero; these are the *s* orbitals with the most eccentric elliptical orbits. In other words, electrons so described deviate most from circular paths, except the *s* electrons in the *K* shell ($n = 1$). An electron with such an orbit approaches the nucleus more closely than an electron with a more circular movement. Therefore electrons in the *s* orbitals have lower energy states (are held more tightly) than *p, d*, and *f* electrons. Consequently it is to be expected that the orbits of the *p, d*, and *f* electrons are successively more circular than *s* electrons, and in successively higher energy states.

An electron moving around the nucleus of an atom in an elliptical orbit, other than a circle, does not travel with uniform velocity. At different times during its rotation it will be either approaching the nucleus or

receding from it. As a result of its movement in this manner the actual velocity of the electron will not be uniform. When the electron is closest to the nucleus, its velocity will be greater than when at the most remote point of the ellipse. The changes in velocity will, according to the theory of relativity, produce accompanying changes in mass; consequently the effective mass will vary with velocity as the electron moves in its elliptical course. Furthermore the change in mass will produce a corresponding,

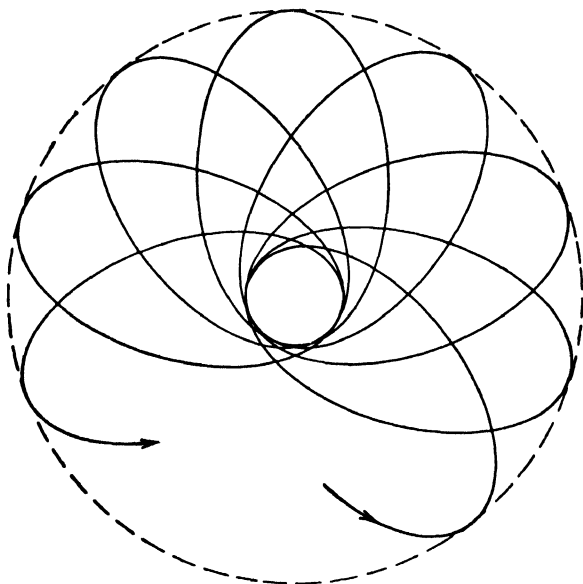


Fig. 2-16 Precession of an elliptic orbit according to the Bohr theory.

although slight, change in the effective coulombic forces operating between the electron and the nucleus. These changes in velocity, effective mass, and effective forces of attraction cause a slow precession in the orbit of the electron so that the major axis of the ellipse changes position in space and the actual path of the electron is a succession of slightly changing orbits, which appear as a rosette pattern when diagrammed. A diagram of this pattern is given in Fig. 2-16.

2-22 The Magnetic Quantum Number. The third quantum number m designates the third degree of freedom of the electron. It describes the orientation of the electronic orbit in space, particularly under the influence of an applied magnetic field. The effect of a magnetic field upon spectral lines was first observed by Zeeman in 1896. When the source emitting the spectral lines is placed in a strong magnetic field and the spectrum examined in a direction at right angles to the field, each

line of the spectrum is split into three components. However, if the lines are viewed in a direction parallel to the magnetic field, only two components are observed. These phenomena would indicate that energy levels are split when the emitting atoms are in a strong magnetic field.

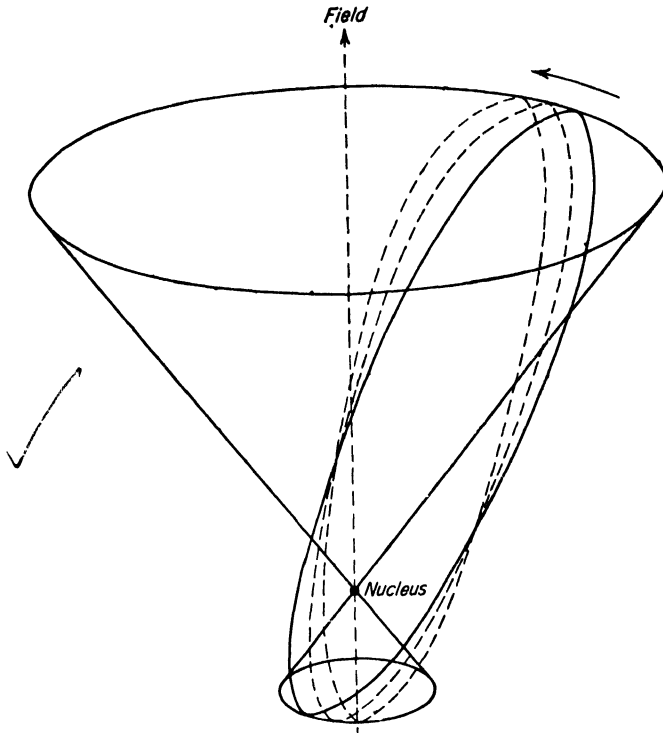


Fig. 2-17 Larmor precession of an electronic orbit in a magnetic field.

To account for these observations by means of the Bohr theory, it was necessary to postulate the third quantum number, known as the *magnetic quantum number*.

Mathematically the third quantum number may be defined by the equation

$$\text{Total angular momentum} = \frac{mh}{2\pi}$$

In the presence of a magnetic field the orbital motion of the electron is disturbed in such a manner that the axis of angular momentum will orient itself to form a definite angle with the direction of the applied field. The orbital angular momentum undergoes a *Larmor precessional motion*,

describing the surfaces of two cones whose axes are in the direction of the field. The Larmor precession of an electronic orbit in a magnetic field is indicated in Fig. 2-17. In this diagram the upper circle represents the path of aphelion and the lower the path of perihelion. The frequency of the precession is proportional to the strength of the magnetic field. Furthermore the electron axis precesses at only certain angles with the direction of the field. This phenomenon is called *space quantization* and is indicated in Fig. 2-18, in which l

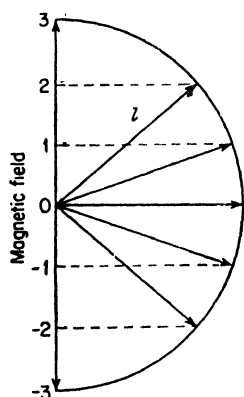


Fig. 2-18 Space quantization in a magnetic field.

represents the axis of angular momentum of the electron and H the external field. The possible angles, or inclinations, at which the vector quantity l may precess about H are given by the relation

$$l \cos \theta = m$$

where m , the magnetic quantum, may have any integral value, including zero from $-l$ to $+l$, giving a total of $2l + 1$ possible values. In Fig. 2-18 the value of l , the azimuthal quantum number, which is also the vector of angular momentum, is taken as 3, and the possible inclinations are seven in all. As the diagram indicates, positive values of m describe orbital-angular-momentum components which are in the direction of the applied magnetic field, and negative values are for those components which are oriented in a direction opposite to that of the field.

2-23 The Spin Quantum Number. The fourth quantum number s denotes the fourth degree of freedom of the electron and is necessary to explain the fine structure of spectral lines within atomic levels. In a magnetic field an electron behaves as if it were spinning rapidly about its own axis. This conclusion is reached as a result of the discovery that the electron, itself, is a tiny magnet, its magnetic field being due to an apparent spin about its own axis. Mathematically the fourth quantum number is defined by the equation

$$mvr = \frac{h \sqrt{s(s+1)}}{2\pi}$$

where mvr denotes angular momentum; and the spin quantum number s may have values of either $+\frac{1}{2}$ or $-\frac{1}{2}$. Inasmuch as a magnetic field is produced by the motion of the electron in its orbit as well as by the electron spinning upon its axis, the total potential energy of the system depends upon the orientation of the electron as a magnet with respect to the orbital motion. For the atoms of those elements which have only

one electron in the outermost orbit the spectral lines are found to be doublets, and it is necessary to assume only two directions of electron spin. The orientation of spin momentum with reference to orbital angular momentum is indicated diagrammatically in Fig. 2-19. The axis of spin is either parallel or antiparallel to the vector designating the direction of the orbital angular momentum of the electron. With this variable it is evident that the spin motion of each electron might strengthen (+) or weaken (−) the orbital energies to a slight extent. This contribution

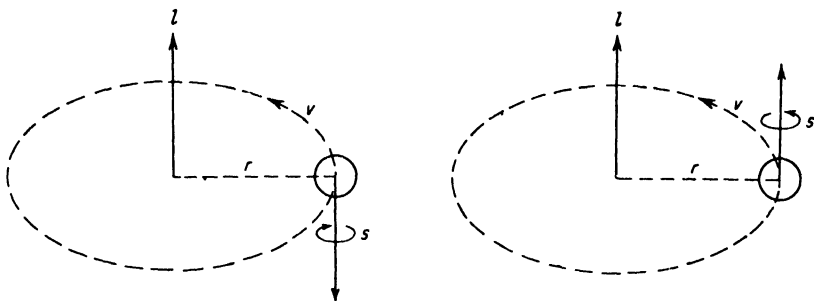


Fig. 2-19 Orientation of spin momentum with reference to orbital angular momentum.

to the total angular momentum is quantized; therefore the spin quantum number is capable of assuming only the two values of $+\frac{1}{2}$ or $-\frac{1}{2}$ in terms of $h/2\pi$ units of angular momentum.

ELECTRON DISTRIBUTION

Four quantum numbers are necessary to describe an electron. These numbers denote its four degrees of freedom and describe its orbit in terms of size, shape, and orientation in space, as well as giving the direction of spin about its axis. This information brings up the questions as to the arrangement and distribution of electrons among the atoms of the various elements. Certain selection principles indicate the distribution of electrons in an atom. The first four are the rules governing the permitted values of the four quantum numbers; the fifth, and controlling one, is referred to as Pauli's exclusion principle.

2-24 Pauli's Exclusion Principle; Distribution of Electrons in Quantum Groups. On the basis of certain spectroscopic evidence W. Pauli in 1925 enunciated his famous rule, which is usually known as the *Pauli exclusion principle*. This rule states that no two electrons in the same atom can have the same values for the four quantum numbers. The basis of this rule is completely empirical; yet its validity is universal. From this rule may be interpreted the possibility of two electrons having orbits of the same size, shape, and orientation in space, provided they are of opposed spins.

106 Fundamental Concepts of Inorganic Chemistry

Two electrons of this description are referred to as *paired* electrons, and such pairing influences the mode in which atoms form chemical bonds.

In accordance with the foregoing selection principles each principal shell of an atom may contain up to four sublevels, or orbits. The possible sublevels are indicated by the small letters *s*, *p*, *d*, and *f*. Each of

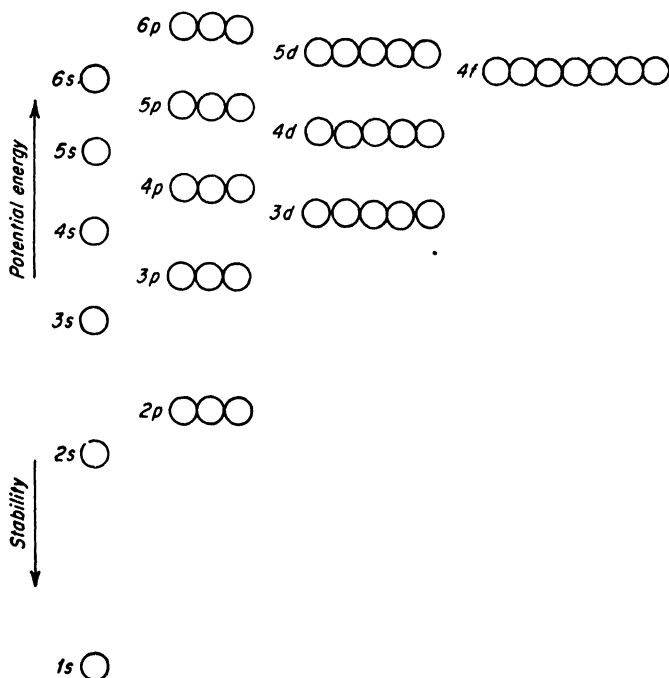


Fig. 2-20 The approximate stability sequence for atomic orbitals. (Linus Pauling, "The Nature of the Chemical Bond," p. 26, Cornell University Press, Ithaca, N.Y., 1940.)

the subshells may contain electrons, up to a definite maximum, as single or paired electrons; however, if two electrons are present, they must be of opposed spins. Two similar orbits (pathways), within a single subshell, constitute an *orbital*. All the various combinations of the four quantum numbers permitted by the exclusion principle are given in Table 2-2.

✓ **2-25 Atomic Orbitals and Energy Levels.** Another method of indicating electron distribution among atoms, used first by Pauling,¹ is portrayed in Fig. 2-20. This diagram gives the order in which shells or subshells (energy levels or sublevels) are filled, and this order is deter-

¹ L. Pauling, "The Nature of the Chemical Bond," 2d ed., p. 26, Cornell University Press, Ithaca, N.Y., 1940.

TABLE 2.2 DISTRIBUTION OF ELECTRONS AMONG THE QUANTUM LEVELS

Principal n	Sub- group	Orbi- tal l	Mag- netic m	Spin s	Sub- total	Total
1	s	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2	2
2	s	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$	6	8
	p	1	0	$+\frac{1}{2}$ $-\frac{1}{2}$		
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$		
			-1	$+\frac{1}{2}$ $-\frac{1}{2}$		
				$+\frac{1}{2}$ $-\frac{1}{2}$		
3	s	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2	18
	p	1	0	$+\frac{1}{2}$ $-\frac{1}{2}$	6	
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$		
			-1	$+\frac{1}{2}$ $-\frac{1}{2}$		
				$+\frac{1}{2}$ $-\frac{1}{2}$		
				$+\frac{1}{2}$ $-\frac{1}{2}$		
	d	2	0	$+\frac{1}{2}$ $-\frac{1}{2}$	10	
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$		
			-1	$+\frac{1}{2}$ $-\frac{1}{2}$		
			+2	$+\frac{1}{2}$ $-\frac{1}{2}$		
			-2	$+\frac{1}{2}$ $-\frac{1}{2}$		
				$+\frac{1}{2}$ $-\frac{1}{2}$		
				$+\frac{1}{2}$ $-\frac{1}{2}$		
			$+\frac{1}{2}$ $-\frac{1}{2}$			
4	s	0	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2	
	p	1	0	$+\frac{1}{2}$ $-\frac{1}{2}$	6	
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$		
			-1	$+\frac{1}{2}$ $-\frac{1}{2}$		
				$+\frac{1}{2}$ $-\frac{1}{2}$		
				$+\frac{1}{2}$ $-\frac{1}{2}$		
	d	2	0	$+\frac{1}{2}$ $-\frac{1}{2}$		
			+1	$+\frac{1}{2}$ $-\frac{1}{2}$		
			$+\frac{1}{2}$ $-\frac{1}{2}$			

TABLE 2-2 DISTRIBUTION OF ELECTRONS AMONG THE QUANTUM LEVELS (Continued)

Principal <i>n</i>	Sub- group	Orbi- tal <i>l</i>	Mag- netic <i>m</i>	Spin <i>s</i>	Sub- total	Total	
	<i>f</i>	3	-1	$+\frac{1}{2}$	10		
				$-\frac{1}{2}$			
			+2	$+\frac{1}{2}$			
				$-\frac{1}{2}$			
			-2	$+\frac{1}{2}$			
				$-\frac{1}{2}$			
			0	$+\frac{1}{2}$			
				$-\frac{1}{2}$			
			+1	$+\frac{1}{2}$			
				$-\frac{1}{2}$			
			-1	$+\frac{1}{2}$			
				$-\frac{1}{2}$			
			+2	$+\frac{1}{2}$	14		
				$-\frac{1}{2}$			
			-2	$+\frac{1}{2}$			
				$-\frac{1}{2}$			
		+3	$+\frac{1}{2}$	14	32		
			$-\frac{1}{2}$				
		-3	$+\frac{1}{2}$				
				$-\frac{1}{2}$			

mined by the relative energies of the respective shells or subshells, the electron always going into the available space of lowest energy. Each principal shell of an atom may contain up to four sublevels, indicated by the lower-case letters *s*, *p*, *d*, and *f*, and each sublevel may contain electrons, up to a definite maximum, as single electrons or paired electrons. If two electrons are present, they must be of opposed spins. From the diagram it may be seen that sublevel *s* of any principal shell can contain only one orbital; sublevel *p*, three orbitals; sublevel *d*, a maximum of five orbitals; and sublevel *f*, up to seven orbitals.

In general the electrons first occupy the energy levels nearest the nucleus. During the process of atom building one electron goes into each possible orbital in a given sublevel until each of the orbitals in that sublevel contains one electron, all single electrons being of parallel spin; then another electron is added to each orbital to form coupled electrons, or paired electrons, until each orbital contains two electrons. The opposed spins of the electrons result in an electromagnetic attraction which is more than sufficient to overcome the electrostatic repulsion of the two negative charges of the same electrons. This explanation is satisfactory for atoms containing very few shells; however, for those

atoms containing many shells, there is considerable overlapping of subshells, and the process of atom building is not nearly so simple as Fig. 2-20 might indicate.

2-26 The Electronic Configuration of the Atoms of the Elements. As a recapitulation of those rules and principles involved in predicting the distribution of electrons among the atoms, we may summarize the knowledge relating to this distribution as follows:

1. The number of electrons distributed about the nucleus of a neutral atom is equal to the atomic number of the atom. The electrons are not distributed at random but are arranged among the known elements in seven main energy levels which are designated by the quantum numbers $n = 1, 2, 3$, etc.

2. The main energy levels are subdivided into minor energy levels. The sublevel energy states result from slight differences in various shapes of the electron orbits and are indicated by the letters s, p, d , and f . However, all main levels do not necessarily have all four of the permissible sublevels; the actual number is indicated by the principal quantum number. Thus, if the quantum number is 1, there is only one sublevel, the s level. If the quantum number is 3, there can be only three sublevels, the s, p , and d levels.

3. The distribution of an electron within a sublevel is described as an orbital, and each orbital may contain either one or two electrons, but if two electrons are present, they must be of opposed spins. The number of orbitals within each sublevel is limited. Only one orbital is possible for the s sublevel, whereas the p may have three, the d may have five, and the f sublevel is limited to seven orbitals.

The distribution of electrons in the atoms of the elements with respect to the quantum numbers of n and l is given in Table 2-3. The values of principal shells as $n = 1, 2, 3$, etc., agree with the designation of the shells as K, L, M , etc. The inert gases are the key elements in this table, since each contains one or more completed shells. According to Table 2-2 completed shells contain electron totals of 2, 8, 18, and 32. The configurations of the atoms of most of the elements in Table 2-3 are based upon experimental observations, mainly from spectral lines. However, the configurations of some of the elements, particularly the post-uranium elements, and a few of the lanthanons, have not as yet been determined experimentally. In such cases the configuration given is that deduced from the position of the element in the periodic classification.

WAVE MECHANICS

In the preceding sections we have discussed atomic structure in terms of the theory introduced by Bohr in 1913. Actually the Bohr theory has

TABLE 2-3 DISTRIBUTION OF ELECTRONS IN THE ATOMS OF THE ELEMENTS

		<i>K</i> 1s	<i>L</i> 2s 2p	<i>M</i> 3s 3p 3d	<i>N</i> 4s 4p 4d 4f	<i>O</i> 5s 5p 5d 5f	<i>P</i> 6s 6p 6d	<i>Q</i> 7s
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	2	2 6	2 3				
S	16	2	2 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	2 6	2 6 3	2			
Cr	24	2	2 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 6	2 6 10	2 6 5	1		

TABLE 2-3 DISTRIBUTION OF ELECTRONS IN THE ATOMS OF THE ELEMENTS (Continued)

		K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p 5d 5f	P 6s 6p 6d	Q 7s
Tc	43	2	2 6	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			
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 6 10	2 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 10	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	
Sm	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	
Dy	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	
Tm	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	

TABLE 2-3 DISTRIBUTION OF ELECTRONS IN THE ATOMS OF THE ELEMENTS (Continued)

		K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p 5d 5f	P 6s 6p 6d	Q 7s
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 6 10 14	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
En	99	2	2 6	2 6 10	2 6 10 14	2 6 10 10	2 6 1	2
Fm	100	2	2 6	2 6 10	2 6 10 14	2 6 10 11	2 6 1	2
Mv	101	2	2 6	2 6 10	2 6 10 14	2 6 10 12	2 6 1	2
Nm(?)	102	2	2 6	2 6 10	2 6 10 14	2 6 10 13	2 6 1	2

long since been superseded by another approach to the problem of atomic structure, which, although harder to visualize, seems to be in complete agreement with experimental information. Although the Bohr model was successful in explaining the observed spectra for hydrogenic atoms and ions, it was inadequate for those atoms having a large number of electrons. Moreover there was no satisfactory justification for the assumption that only those orbits are permitted for which the angular momentum is equal to some integral multiple of $h/2\pi$. Another unsatisfactory aspect of the Bohr model was its attempt to assign, simultaneously, an exact position and a definite momentum to a given electron. We now believe, according to the Heisenberg uncertainty principle, that it is impossible to determine at the same time the position and momentum of particles such as electrons and neutrons.

The modern theory of atomic structure is based on the wave nature of the electron. This more satisfactory theory, which is called *wave mechanics*, was developed principally by L. de Broglie, E. Schrödinger, and W. Heisenberg. Their approach to the problem of atomic structure is highly mathematical and, for that reason, beyond the scope of this book. We shall attempt only to bring out the main ideas in a non-

mathematical way and to describe some of the experimental evidence for the wave nature of electrons and other material particles.

2.27 The Wave Theory of Matter. In 1924 L. de Broglie suggested that any moving material particle has associated wave properties. He conceived the idea from Einstein's earlier suggestion that light quanta have properties of matter, among which one is momentum. From this suggestion De Broglie deduced that the laws of optics differ from the laws of ordinary mechanics only because the rest mass of photons is zero.

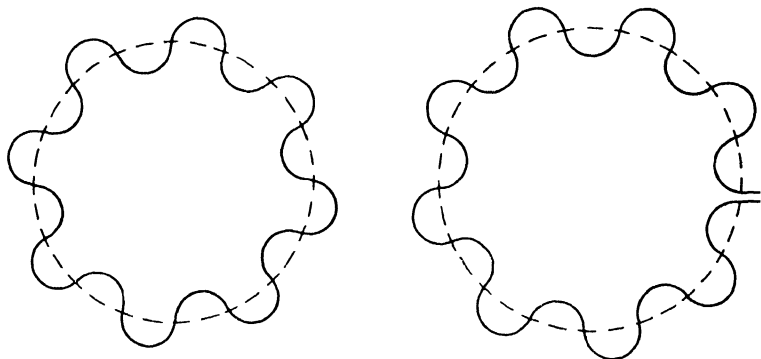


Fig. 2.21 Diagrammatic representation of electron orbitals, one of which is in phase, and the other out of phase.

Hence, De Broglie reasoned, particles with small masses, such as electrons, should behave somewhat similarly to photons with zero masses. Therefore he began with the assumption that every kind of material particle which is moving is carried by means of waves that are propagated in space according to laws similar to those obeyed by light waves. The wavelength associated with a moving particle is given by the equation

$$\lambda = \frac{h}{mv} \quad (2.19)$$

where λ is the wavelength, h is Planck's constant, m is mass, and v is the velocity of the particle. Then, if r is the radius and $2\pi r$ the circumference of the circle occupied by the wave, we have

$$\lambda n = 2\pi r \quad (2.20)$$

According to this theory the electron is no longer a point mass moving in an orbit but is, instead, a standing wave train extending around the nucleus in a circular form. The vibrations within the wave must be in phase to come out equal, and the circumference on the circle occupied by the wave must include some integral number of wavelengths. The general idea of electron waves, in phase and out of phase, is portrayed in Fig. 2.21.

114 Fundamental Concepts of Inorganic Chemistry

Since the circumference must contain an integral number of wavelengths, the value n will be 1, 2, 3, etc.; therefore, Eqs. (2.19) and (2.20) may be combined as

$$2\pi r = n \frac{h}{mv} \quad (2.21)$$

or, upon rearranging,
$$mvr = n \frac{h}{2\pi} \quad (2.22)$$

It will be recalled that mvr is the angular momentum of the electron, and the wave-mechanical picture of De Broglie reaffirms Bohr's postulate that the angular momentum must be an integral multiple of $h/2\pi$.

De Broglie's idea of material particles traveling in waves was verified in 1927 by C. J. Davisson and L. H. Germer, who, while working in the Bell Telephone Laboratories, discovered that a beam of electrons underwent diffraction by a crystal lattice, in the same manner as a beam of X rays. In their experiment Davisson and Germer used the surface of a crystal of nickel as a diffraction grating and computed the wavelengths in the beam from their known velocities. Their results indicated that the electrons behaved more like waves than particles and that the angles at which strong reflection took place were the same as those at which X rays of the same wavelength would be reflected.

Further verification of the wave nature of particles was obtained by G. P. Thomson of England and S. Kikuchi of Japan, who obtained Laue diffraction patterns by passing fast-moving electrons through thin sheets of metal and mica and then allowing the resulting beam to fall on a photographic plate.

2.28 The Uncertainty Principle. In 1927 Werner Heisenberg of Germany enunciated one of the most fundamental relationships of modern physics, which has become known as the *uncertainty principle*. According to this principle it is impossible to make, simultaneously, the exact determination of the velocity of a particle and also its position. The uncertainties in the determinations of these two quantities vary inversely, so that, if one is determined fairly accurately, the other must be correspondingly less accurate. This limitation is in no way dependent upon the accuracy of the observing instruments or the methods of measurements; it is an inherent relationship in nature. Actually the indeterminism results from the interaction of the particle or wave under observation with the measuring system. For example, we either add or subtract energy to or from a system in the process of observing it, and if the system involves a very small particle, it will undergo a change in momentum or a change in position.

In the case of the electron the product of the uncertainty of position and the uncertainty of velocity is proportional to the Planck constant.

Furthermore the product of these two uncertainties cannot be smaller than $h/2\pi$. In other words, we cannot localize an electron without giving it a high momentum. On the other hand, if the wave properties of an electron are known from diffraction measurements, the uncertainty of its position will have been increased.

2.29 The Schrödinger Wave Equation. In following the idea, put forward by De Broglie, that wave properties are associated with material particles E. Schrödinger developed a wave equation for particles that is very similar to the wave equations of optics and acoustics. This equation is a partial differential whose solution yields the electron distribution in space as well as the allowed energy levels of a particle moving in a given field. One form of the equation is

$$\nabla^2 u + \frac{8\pi^2 m}{h^2} (E - V)u = 0 \quad (2.23)$$

in which ∇^2 is the Laplacian operator, u is the amplitude function for the three coordinates of the particle, m is the mass of the particle, h is Planck's constant, and E and V are the total and potential energies. The wave function associated, in the De Broglie sense, with the orbital motion of the electron is usually referred to simply as its orbital. The probability of finding the electron at a certain point may be determined by evaluating the quantity u^2 . The plots of electron density found in Sec. 4.13 in a discussion of chemical bonding result from a computation of u^2 for a particular arrangement of electrons in a particular atom using the foregoing equation.

To obtain the Schrödinger equation in the form given in the preceding paragraph, it is possible to start with the fundamental equation for harmonic wave propagation in any medium. The equation is perfectly general in form, equally applicable to acoustic waves in water, compressional waves in steel, or light waves in a vacuum. This more basic equation, as found in most books on theoretical physics, takes the form of a partial differential equation of the second order,

$$\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} + \frac{\partial^2 U}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 U}{\partial t^2} \quad (2.24)$$

where U is the displacement of the waves and c is the velocity of the waves in the medium, for our purpose the velocity of light. The representation is that of the displacement U , in the three cartesian coordinates x , y , and z as a function of time t . Since the only solutions of the equation which have physical significance are those where U is a function of time, we may rewrite U in the exponential form, so that

$$U = ue^{2\pi i t} \quad (2.25)$$

116 Fundamental Concepts of Inorganic Chemistry

where u is the amplitude of the waves, a function of x , y , and z , but not a function of time, as was U in the previous equation. The frequency of the wave function is ν , i is the quantity $\sqrt{-1}$, and t is time. To reach Schrödinger's equation, three differentiations must be performed, as follows:

$$\frac{\partial U}{\partial t} = u(2\pi\nu i)e^{2\pi\nu i t} \quad (2.26)$$

$$\frac{\partial^2 U}{\partial t^2} = u(2\pi\nu i)^2 e^{2\pi\nu i t} = -4\pi^2\nu^2 u e^{2\pi\nu i t} \quad (2.27)$$

$$\begin{aligned} \frac{\partial^2 U}{\partial x^2} &= e^{2\pi\nu i t} \frac{\partial^2 u}{\partial x^2} \\ \frac{\partial^2 U}{\partial y^2} &= e^{2\pi\nu i t} \frac{\partial^2 u}{\partial y^2} \\ \frac{\partial^2 U}{\partial z^2} &= e^{2\pi\nu i t} \frac{\partial^2 u}{\partial z^2} \end{aligned} \quad (2.28)$$

Any student of elementary calculus can accomplish these differentiations. If we now substitute these identities into Eq. (2.24), the result is

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = -\frac{4\pi^2\nu^2}{c^2} u \quad (2.29)$$

Since the wavelength and frequency of any wave are related by the expression $\lambda = c/\nu$, we may substitute $\lambda^2 = c^2/\nu^2$ above to obtain

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = -\frac{4\pi^2}{\lambda^2} u \quad (2.30)$$

There is nothing remotely related to atoms or electrons in this equation. However, using the De Broglie relation $\lambda = h/mv$ from Sec. 2.27, we note that the right-hand side of the equation may be rewritten

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = -4\pi^2 \frac{m^2 v^2}{h^2} u \quad (2.31)$$

We may write the right-hand member of the equation in slightly different form,

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = -\frac{8\pi^2 m}{h^2} \frac{mv^2}{2} u \quad (2.32)$$

to emphasize that kinetic energy, $mv^2/2$, is involved. We can also substitute the equivalent expression

$$\text{Kinetic energy} = \frac{mv^2}{2} = E - V \quad (2.33)$$

where the total energy is E and the potential energy is V . Clearly total

energy E equals the sum of the kinetic and potential energies. Then, substituting, we have

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)u = 0 \quad (2.34)$$

which is identical with the expression for Schrödinger's equation (2.23), where the differential functions of u have been abbreviated by the mathematical symbol $\nabla^2 u$. In many treatments the symbol ψ is used instead of u , but the significance is the same.

The wave-mechanical model considers the mass and charge of the electrons as distributed about the nucleus in three dimensions, and not confined to plane orbits as in the Bohr atom. It is difficult to produce any physical interpretation of the Schrödinger equation. Apparently the mathematics of the atom is beyond physical meaning in terms of ordinary human comprehension. Some writers have attempted to describe an electron as a cloud or a smear which acts as an envelope around the nucleus, but such a description raises more questions than it answers. The dualistic nature of the electron, in which it may be represented as both a particle and a wave, represents an overwhelming obstacle to either a verbal or a diagrammatic description as to the manner in which electrons are distributed within an atom. Recently, however, photons, discussed in Sec. 1.3, have been suggested as the means by which energies are exchanged between electrons in much the same manner as pi mesons serve to exchange energy between protons and neutrons. Since photons are ordinarily treated as if they were waves, it may be sufficient to wind up our discussion of atomic structure by saying that an atom is now visualized as a region without definite boundaries through which electrons are spread in the form of particle waves whose densities may be described by means of probability-distribution curves. We need not be unduly disturbed by the apparent duality, of wavelike as well as particle nature, of the electron.

EXERCISES

1. What is meant by the atomic number of an element? Upon what experimental basis have atomic numbers been assigned to the elements?
2. How are X-ray frequencies related to atomic numbers?
3. What is the relation of atomic numbers to the periodic classification of the elements?
4. What is the relation between Planck's constant and the photoelectric effect?
5. What is meant by an excited atom? How may an atom be excited?
6. What is the difference between a continuous spectrum and a discontinuous one?
7. Explain the presence of so many lines in the hydrogen spectrum, even though hydrogen contains only one electron.

118 Fundamental Concepts of Inorganic Chemistry

8. Why does atomic hydrogen emit light as a line spectrum rather than a continuous spectrum?

9. Why is the size of a quanta of ultraviolet light greater than that of the infrared?

10. Calculate the wavelengths of the $H\alpha$, $H\beta$, and $H\gamma$ lines, using the value of the Rydberg constant as $109,300\text{ cm}^{-1}$.

11. From the wavelength of $H\alpha$ in Table 2-1 calculate the Rydberg constant for hydrogen.

12. Calculate the wavelengths for the longest and the shortest waves in the Lyman and Paschen series of atomic hydrogen.

13. What is the relation between the energy of a quantum and the frequency of the radiation?

14. Show that Planck's constant has the dimensions of angular momentum.

15. How did Bohr explain the process by which the hydrogen atom may emit light?

16. In terms of the Bohr theory what does the spectra seem to indicate with respect to the location of electrons in the atoms of the elements?

17. Explain the relationship between energy levels and the frequencies of the lines in the spectra of atomic hydrogen.

18. Show that the circumference of a stable Bohr orbit is a multiple of the wavelength of the electron in the wave-mechanics orbital.

19. Calculate the circumference of the eighth Bohr orbit.

20. What are the radius of the third Bohr orbit and the velocity of an electron in this orbit?

21. Compare the velocity of the electron in the first principal energy level of the hydrogen atom with the velocity of light.

22. Why does an electron have more energy in the second orbital level of the hydrogen atom than it has in the first?

23. How much energy is necessary to remove an electron from the second Bohr orbit of a hydrogenic atom so that it is outside the influence of the nucleus?

24. Why does it require less energy to move an electron from the second to the third energy level of the hydrogen atom than it does from the first to the second?

25. How would you expect the spectrum of singly ionized helium to be different from that of the hydrogen atom?

26. Derive the expression for the kinetic energy of an electron in a Bohr orbit.

27. According to the Bohr theory how is the size of an orbit related to the principal quantum number?

28. State the meaning of the four quantum numbers required to describe an electron.

29. What is Pauli's exclusion principle? How many electrons may exist in the M shell of an atom when this shell is complete? How are these electrons distributed within the shell?

30. What is meant by energy level in an atom? What is the maximum number of electrons which each energy level of an atom can accommodate?

31. How many electrons are there in the valency quantum level of the bromine atom?

32. Show the distribution of electrons around the nucleus of an atom of the

element with atomic number of 20; with atomic number of 36; with atomic number of 27.

33. What is the difference between an orbit and an orbital? How many orbitals are there in the *d* sublevel? In the *f* sublevel?

34. What is the total energy of an electron whose De Broglie wavelength is 1.2×10^{-8} cm?

35. What is the wavelength of a hydrogen atom moving with a velocity of 2000 m/sec?

36. Calculate the wavelength of a body with a mass of 10 mg and which is moving with a velocity of 100 cm/sec.

37. Why, according to the Heisenberg uncertainty principle, is it impossible to measure simultaneously the position and momentum of a fast-moving small body?

38. Does the Heisenberg uncertainty principle apply to the determination of the positions and velocities of the planets in our solar system?

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CHAPTER 3

Classification of the Elements

During the nineteenth century much time and effort on the part of chemists were devoted to seeking an arrangement for the known elements which would emphasize similarities in properties and thereby facilitate their systematic study. The culmination of this search was the discovery of the *periodic law*, which may be concisely stated as follows: *The properties of the elements are periodic functions of their atomic weights.* The formulation of this law has been attributed by many writers to Dmitri Mendeleev, but most certainly the same idea was also expressed in the writings of both Beguyer de Chancourtois and John Newlands. The discovery of this law permitted an orderly classification of the elements and a prediction of certain missing elements. The use of a periodic system for the methodical arrangement of the elements has made it possible for students to assimilate a great deal of knowledge about all the elements by studying the general properties of groups of related elements. Since all the missing elements have been discovered, the periodic system is no longer a guide in this respect. However, its use in teaching the properties of the various different atoms and their ions, in relation to their positions in such a classification, will always be important. For this reason it is worthwhile to trace the history and development of the methods of classification and to examine some of the more important present-day periodic systems for the elements.

HISTORICAL

The earliest attempts to classify elements date back to the discovery of metals and the recognition that such substances were elementary in character. According to an early classification metals were divided into those which were noble and those which were base. The former included gold and silver and the latter copper, iron, lead, tin, and mercury. However, it was not until after the establishment of the atomic theory of Dalton that chemists became concerned to seek a relation between the properties of the elements and their atomic weights. In 1815 William

Prout suggested that the atomic weights of all the elements were exact multiples of the atomic weight of hydrogen. Although this theory was disproved by subsequent accurate determinations of atomic weights, it did represent one of the first attempts to correlate the structure of matter with atomic weights.

3-1 Döbereiner's Triads. The first recognition of a significant relation between the atomic weights and the properties of the elements was noted by Johann Wolfgang Döbereiner. In 1817 Döbereiner observed

TABLE 3-1 DOBEREINER'S TRIADS

Triad	Atomic weights	Average of first and third element	Difference between consecutive elements
Calcium..	40 08	88 72	47 55 49 73
Strontium	87 63		
Barium.	137 36		
Lithium	6 940	23 020	16 057 16 103
Sodium	22 997		
Potassium	39 100		
Sulfur	32 066	79 84	46 85 48 65
Selenium	78 96		
Tellurium	127 61		
Chlorine	35 457	81 183	44 459 46 994
Bromine	79 916		
Iodine.	126 91		

that several groups of three closely related elements, which he called *triads*, existed in which the central, or middle, element had an atomic weight almost the arithmetical mean of the other two elements. Moreover the differences between the atomic weights of the three related elements were approximately constant.

Among the groups of elements indicated as triads by Döbereiner were: calcium, strontium, and barium; lithium, sodium, and potassium; sulfur, selenium, and tellurium; and chlorine, bromine, and iodine. Using present-day atomic weights, which are more accurate than those of the time of Döbereiner, the numerical relationships existing in the so-called triads are indicated in Table 3-1.

The apparent regularity in atomic weight averages and differences, indicated by the elements of Döbereiner's triads, stimulated other investigators to seek additional and wider numerical relationships. However, the many attempts to classify the elements prior to 1858 failed, largely because atomic weights were not evaluated on a sound basis. In 1858

Stanislao Cannizzaro published his "Sketch of a Course of Chemical Philosophy," in which he established the relations among equivalent weight, atomic weight, and molecular weight upon the basis of Avogadro's hypothesis. It was after the publication of this treatise that the

real advances in the classification of the elements were made.

3.2 The Telluric Screw of De Chancourtois. The first truly periodic arrangement of the elements should be credited to Beguyer de Chancourtois. It was in 1863 that Chancourtois, an engineer and a geologist, published the first of a series of papers in which he emphasized the fact that when the elements are arranged in the order of their ascending atomic weights there is a recurrence of elements with similar properties. De Chancourtois plotted the values of the atomic weights on a helical curve described on a vertical cylinder. The convex surface of the cylinder was divided into 16 equal parts, with lines drawn parallel to the axis. The number 16 was selected because it represented the atomic weight of oxygen. The curve was drawn by starting at the base and ascending the cylinder at an angle of 45° . In this graphic representation each intersection of the spiral curve with one of the vertical lines represented a unit of atomic weight, and each crossing of

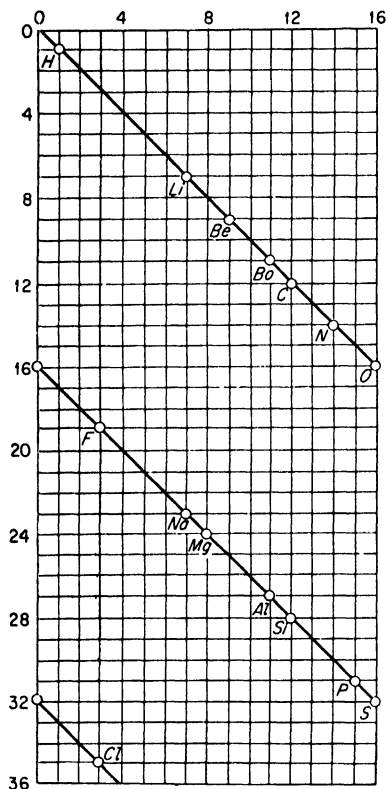


Fig. 3-1 An unfolded portion of De Chancourtois' telluric screw.

a given generatrix was a multiple of 16. This curve, which De Chancourtois called the *telluric screw*, produced an arrangement whereby related elements fell upon the same vertical line. An "unfolded" portion of the telluric screw is given in Fig. 3-1. The similarity among vertically arranged elements caused De Chancourtois to suggest that "the properties of substances are properties of numbers."

3.3 Newlands' Law of Octaves. Without knowledge of De Chancourtois' work a somewhat similar system of classification for the elements was developed by John A. R. Newlands in England between 1863 and

1865. Upon arranging the known elements in the order of their atomic weights, he noticed that in many cases there was a repetition of chemical properties in each eighth element. Elaborating on this idea, he published a series of papers in the *Chemical News* during this period. In one of these papers he stated: "The difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music."

In 1866 Newlands delivered a paper entitled "On the Law of Octaves" before the Chemical Society of London. In this paper he proclaimed his

TABLE 3-2 NEWLANDS' TABLE OF THE ELEMENTS IN OCTAVES*

H... .. 1	F 8	Cl 15	Co and Ni... 22
Li... .. 2	Na 9	K 16	Cu... .. 23
G 3	Mg 10	Ca 17	Zn 24
Bo. . . . 4	Al 11	Cr 18	Y... .. 25
C... .. 5	Si 12	Ti 19	In... .. 26
N... .. 6	P 13	Mn 20	As. . . . 27
O... .. 7	S 14	Fe 21	Se 28
Br. . . . 29	Pd 36	Te 32	Pt and Ir. . . 50
Rb. . . . 30	Ag 37	Cs 44	Os 51
Sr 31	Cd. . . . 38	Ba and V . . . 45	Hg 52
Ce and La. . 32	U 39	Ta 46	Tl 53
Zr 33	Sn. . . . 40	W 47	Pb 54
Di and Mo... 34	Sb 41	Nb 48	Bi 55
Ro and Ru . 35	I 42	Au... .. 49	Th. . . . 56

* J. A. R. Newlands, *Chem. News*, 12: 83 (1865).

discovery of the numerical relationship among the elements to be a law which he termed the *law of octaves*. However, his comparison of the recurrence of chemical properties among the elements with the repetition of musical notes in an octave was unfortunate. His paper was received with ridicule and derision by members of the Chemical Society, and they refused to permit his paper to be published in the journal of this scientific organization. It is said that one member, G. C. Foster by name, asked Newlands sarcastically "whether he had ever examined the elements according to the order of their initial letters." As a lesson in the history of science it might be added that Professor Foster's foolish question is the only reason that his name is still remembered.

Newlands' arrangement of the elements as it appeared in the *Chemical News* is reproduced in Table 3-2. This classification was obviously imperfect. It provided no spaces for elements still to be discovered. Several of the heavier elements were transposed to account for chemical similarities, and some elements, which had no apparent connection with

one another, were placed in corresponding positions in different octaves. Despite the table's many serious defects it did indicate more clearly than any other previous work the recurrence of similar properties among the elements. In 1887 the Royal Society awarded Newlands the Davy medal for his discovery of the periodicity existing among the elements.

3.4 Lothar Meyer. Credit for the development of the periodic system of the elements is usually given jointly to Lothar Meyer of Germany and Dimitri Mendeleev of Russia. Meyer seems to have arrived at his classification through an analysis of those relations among the elements which were based upon their physical properties, whereas Mendeleev appears to have been more influenced by the relations exhibited as chemical properties.

The first edition of Lothar Meyer's well-known textbook "*Moderne Theorien der Chemie*" was published in 1864. This book contained an incomplete periodic table in which the elements were arranged horizontally according to their atomic weights, and in such a manner that elements with similar properties and valence fell under one another. In 1870 Meyer published an expanded version of this table in an article¹ entitled "Nature of the Elements as Functions of Their Atomic Weights." The latter table differed from the first in that the consecutive atomic weights were not arranged horizontally but vertically.

Meyer's periodic system was probably developed a little earlier than the one published by Mendeleev, and in many respects the two tables are almost identical. However, the views expressed by Meyer in his publications indicate that he had a much less clear picture as to the nature of the periodicity among the elements than did Mendeleev. He failed to recognize the importance of differentiating the elements into even and odd series, and his first table made no provision for a separate grouping for the transition elements.

Meyer is less remembered for his periodic table than for the curves he drew, which indicated that certain physical properties such as fusibility, volatility, malleability, and brittleness are periodic functions. This physical periodicity is shown in a modern version of one of his curves given in Fig. 3-4.

3.5 Dimitri Mendeleev. In March, 1869, Mendeleev transmitted to the Russian Chemical Society his first paper on the classification of the elements, which bore the title "The Relation of the Properties to the Atomic Weights of the Elements." This table was published in Russian, from which the English version is reproduced in Table 3-3. Similar elements within this classification were arranged horizontally, which seemed to be the customary arrangement in the earlier tables. Mendeleev's first periodic system was practically identical with those proposed by New-

¹ L. Meyer, *Ann.*, Supplementband VII, 354 (1870).

lands and Meyer, although it is fairly certain that all three systems were original and independent of each other. The superiority and difference in the Mendeleev table over all previous and contemporary tables were its predictions that certain atomic weights had been incorrectly determined and that new elements would be discovered to fit into vacant spaces occurring in the classification. These predictions are indicated in the table by question marks.

TABLE 3-3 MENDELEEV'S TABLE OF THE ELEMENTS (1869)*

H = 1			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104 4	Ir = 197.4
			Fe = 56	Ru = 104 4	Ir = 198
			Ni = Co = 59	Pd = 106 6	Os = 199
			Cu = 63 4	Ag = 108	Hg = 200
			Zn = 65 2	Cd = 112	
			? = 68	Ur = 116	Au = 197?
			? = 70	Sn = 118	
Li = 7	Be = 9 4	Mg = 24	As = 75	Sb = 122	Bi = 210?
	B = 11	Al = 27 4	Se = 79 4	Te = 128	
	C = 12	Si = 28	Br = 80	J = 127	
	N = 14	P = 31	Rb = 85.4	Cs = 133	Tl = 204
	O = 16	S = 32	Sr = 87.6	Ba = 137	Pb = 207
	F = 19	Cl = 35 5	Ce = 92		
	Na = 23	K = 39	La = 94		
		Ca = 40	Di = 95		
		? = 45	Th = 118?		
		?Er = 56			
		?Yt = 60			
		?In = 75 6			

* D Mendeleev, *J. Russ. Chem. Soc.*, 1: 60 (1869).

Mendeleev's first paper also contained certain conclusions he had reached concerning the periodicity of the elements, and these statements may be regarded as containing the fundamental principles of the *periodic law*. In view of the meager, and somewhat inaccurate, chemical information available to Mendeleev in 1869 the extent of his knowledge as to the properties of the elements is no less than amazing. For that reason, it seems worthwhile to include these conclusions, which have been translated¹ as follows:

1. The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties.

2. Elements which are similar as regards their chemical properties have atomic weights which either are of nearly the same value (e.g., platinum, iridium, osmium) or increase regularly (e.g., potassium, rubidium, cesium).

¹ F. P. Venable, "The Development of the Periodic Law," pp. 91-92, Chemical Publishing Company, Easton, Pa., 1896.

TABLE 3-4 MENDELEEV'S TABLE OF 1871

Se- ries	Group I R ₂ O	Group II RO	Group III R ₂ O ₃	Group IV RH ₄ RO ₂	Group V RH ₃ R ₂ O ₃	Group VI RH ₂ RO ₃	Group VII RH R ₂ O ₇	Group VIII RO ₄
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	* = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59 Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	* = 68	* = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Y = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104 Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	*			
9		...	?Er = 178	?La = 180	Ta = 182	W = 184	...	Os = 195, Ir = 197 Pt = 198, Au = 199
10								
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	U = 240		
12				Th = 231				

* Dashes indicate predicted elements, dots signify missing elements.

3. The arrangement of the elements, or groups of elements, in the order of their atomic weights corresponds to their so-called "valences" as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in the series of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.

4. The elements which are most widely diffused have small atomic weights.

5. The magnitude of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.

TABLE 3 5 MENDELEEV'S PREDICTIONS VERSUS OBSERVED PROPERTIES FOR
AN ELEMENT

Property	Predicted for ekasilicon 1871	Observed for germanium 1886
Atomic weight	72 0	72 3
Specific gravity	5.5	5 469
Atomic volume	13 0 cc	13 22 cc
Color	Dark gray	Grayish white
Specific gravity of oxide	4.7	4 703
Boiling point of chloride	100°C	86°C
Specific gravity of chloride	1 9	1 887
Boiling point of ethyl derivative	160°C	160°C
Specific gravity of ethyl derivative	0 96	1 0

6. We must expect the discovery of many yet unknown elements, for example, elements analogous to aluminum and silicon, whose atomic weights would be between 65 and 75.

7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus the atomic weight of tellurium must lie between 123 and 126 and cannot be 128.

8. Certain characteristic properties of the elements can be foretold from their atomic weights.

An improved version of Mendeleev's table appeared in 1871 in which the arrangement of the elements was altered to the now familiar form of vertical groups and horizontal series. In this table, reproduced in Table 3-4, emphasis is laid on the relationship between atomic weight and chemical properties, including valency. Members of the main groups, for the first time, were divided into two subgroups, the division being based largely upon whether the members of the subclasses belonged to series with odd or with even number. For instance, Group II is composed of two subgroups, the first of which contains beryllium, calcium,

strontium, and barium in the series of even number and the second magnesium, zinc, cadmium, and mercury in the series of odd number.

In his writings Mendeleev not only presented the best periodic table of his time, but he made so bold as to venture into the field of prophecy and not only predicted that certain new elements would be discovered to fit into vacant spaces in his system but even foretold with incredible accuracy the properties of some of the undiscovered elements. Three of these elements, which he designated as ekaboron, ekaaluminum, and ekasilicon, were discovered soon after and are now known as scandium, gallium, and germanium. Table 3-5 presents a comparison of Mendeleev's predictions, with the actual determined properties for one of these elements.

MODERN PERIODIC ARRANGEMENTS

In accordance with one of the conclusions which make up his statement of the periodic law Mendeleev used his periodic table to verify the atomic weights of a number of elements that apparently did not fit into the system. Among the atomic weights which he asserted had been incorrectly determined were those of uranium, titanium, and indium. Later determinations of these atomic weights verified these assertions.

Probably every teacher of chemistry has experienced some dissatisfaction with the periodic tables of the elements which are to be found in the various textbooks. It is also likely that a sizable percentage of these teachers have attempted to improve on the more widely accepted periodic arrangements. Many of these proposed classifications have appeared in the chemical literature. It would not be an exaggeration to say that hundreds of different arrangements have been devised in an attempt to show all the various relationships, real and imaginary, that exist among the chemical elements. The majority of these efforts, although sometimes of interest to an advanced student, have been of little practical use.

3-6 Introduction. Originally the periodic classification of the elements served three purposes: (1) it was useful in the verification of atomic weights; (2) it served as a guide in the prediction of undiscovered elements; and (3) it was a systematic correlation of chemical and physical properties of groups of elements, which permitted a student to study these groups rather than individual elements. Of these past uses only the last one still serves a needful purpose. Consequently about the only real excuse for present-day periodic tables is to facilitate the assimilation of chemical facts and relations by chemistry students. Viewed in this light, the usefulness of a periodic table may be evaluated largely by its simplicity and the extent to which it indicates the most important periodic relationship among the elements.

All two-dimensional periodic tables are more or less imperfect since two dimensions do not permit an arrangement showing all the possible periodic resemblances existing among the elements. Three-dimensional models, although of interest, are too unwieldy for most instructional purposes. Since it is impossible to show all the relationships in a simple form, it seems preferable to indicate only the most fundamental periodic properties. On the following pages are presented four tables which are found most frequently in elementary textbooks. Each has certain advantages and disadvantages, which will be pointed out in our discussion.

3-7 Electron Grouping in Atoms. Before proceeding with the description of the more common periodic tables it seems appropriate to list the types of atoms which are recognized in all schemes of classification. This listing emphasizes the fact that the chemical properties of the elements depend upon the extent to which their electron shells are completed (Table 2-3). By the completion of a shell we mean the agreement between the number of electrons it contains and the number in the corresponding shell of the noble gas of the next higher or lower atomic number. A description of the distribution of electrons among the possible quantum levels has been given in Secs. 2-24ff. The symbolic representation of various electronic configurations is illustrated in Sec. 4-3. Upon the basis of complete and incomplete electron shells four types of atoms are recognized.

Type I. Atoms in which the s and p sublevels are complete. The Pauli exclusion principle predicts that the s level can accommodate not more than 2 electrons and the p level not more than 6 electrons. When these levels are complete, the outer shell has a configuration of ns^2np^6 , except for helium, in which the configuration is $1s^2$. These are the atoms of the noble, or inert, gas elements, which have attained an electronic stability which cannot be increased either by electron transfer or by sharing. Because of the stability of their electronic configurations such elements do not enter into ordinary chemical reactions. These elements make up Group 0 of the periodic table.

Type II. Atoms in which all but the highest quantum group (outermost shell) are complete. The electronic configurations in the outer shells of atoms of these elements include any structures from ns^1 through ns^2np^5 . A comparison of Table 2-3, which shows the distribution of electrons in the atoms of the elements, with the Mendeleev periodic grouping as shown in Table 3-6 indicates a relationship between the quantum mechanically permitted orbitals and the placement of elements in the periodic table. For example, the elements of Group IA have an incomplete s level in the outer electronic shell, the elements of Group IIA have a completed s level, and the atoms of the elements of Groups IIIB to VIIB have incomplete p levels in the highest quantum group. Elements

of this type of atom tend to enter into chemical combination through losing, gaining, or sharing electrons, in such wise as to attain the electronic configuration of ns^2np^6 for the outermost shell, which is the same as that found in the noble gases. Many of the elements most often encountered belong to this type. Because of the frequency of their occurrence they are sometimes called the "representative" elements, although such a designation is more or less of a misnomer. The forces operating between their atoms are discussed in detail in Chap. 4.

Type III. Atoms in which the *two* outermost shells are incomplete. They are atoms of those elements in which an inner *d* level is present but not completed. The electronic configurations for the outer shells of these elements include those with a general structure of $(n-1)d^{1-9}ns^{1-2}$. In other words, the next to the outer shell has a *d* level which may contain one through nine electrons, and the outer shell contains either one or two electrons. Elements with atoms of this general structure have been named *transition* elements. The transition series occurring among the elements are those with incomplete *3d*, *4d*, *5d*, and perhaps *6d* orbitals. In the periodic table these elements begin with Group IIIA (Table 3-7) and continue through Group IIB. However, the elements of Group IB (the copper family) and Group IIB (the zinc family) have electronic structures similar to the Type II atoms, but in terms of chemical behavior they have characteristics that are analogous to the transition elements. Because of their electronic structure the transition elements exhibit variable valence. Their tendency to form *coordination compounds* is discussed in Chap. 5.

Type IV. The atoms of elements of this type are actually transition elements, but they differ from atoms of the regular transition elements in that they have *three* outermost shells which are incomplete. They may be more properly identified as *inner transition* elements, inasmuch as they not only have incomplete *d* levels but also *f* levels that have not been filled to capacity. These are the elements of the *rare earth*, or *lanthanide*, series (atomic numbers 58 to 71) and those of the *actinide* series (atomic numbers 90 to 102). We shall have occasion to mention the lanthanide series again in Sec. 3-13. A considerable portion of Chap. 8 is devoted to the transuranic elements which fall in the actinide series. At present it suffices to say that the elements within each of these groups are very similar in their chemical properties because the differentiating electrons of their atoms are in the third from the outermost shell. Because of the similarity of chemical behavior among the elements of the two inner transition series they cannot be accommodated in the conventional periodic tables. Hence it is customary to indicate the two inner transition series as separate groups of elements (Tables 3-6 and 3-7).

3-8 The Modern Mendeleev Periodic Table. As has been intimated earlier in this chapter, it is quite likely that too much credit has been given to Mendeleev for the development of the first widely accepted periodic table, but there is no doubt that the table attributed to him has been the forerunner of all other worthwhile systems of classification for the elements. Acknowledgedly it has many faults, some of which we shall point out later, but so have all periodic tables. Furthermore the majority of modern classifications are the results of attempts to correct these recognized faults. On the other hand the Mendeleev table is superior to all other tables in one respect, and that is its simplicity. We have said in the previous section that the sole purpose of a periodic table is as a valuable tool in the teaching of chemistry. Undoubtedly other forms of the periodic table are more meaningful, but for a beginning student it is probable that the Mendeleev table will always be of value.

A modern version of Mendeleev's periodic table is given in Table 3-6. An examination of this table discloses that it is divided horizontally into *periods*—rows across the table from left to right—whereas, vertically, it is divided into columns called *groups*. There are in all seven periods, of which the first is unique in that it is occupied by only one element, hydrogen. Each of the next two periods contains 8 elements, arranged in a single row called a *short period*, across the table. Following these are two *long periods*, containing 18 elements each, arranged in the form of two rows across the table. The sixth is a very *long period*, consisting of 32 elements, 15 of which are the so-called "rare earths." The seventh and last period appears incomplete, inasmuch as it contains the actinide series of elements, all of which, as yet, have not been discovered.

The vertical columns are occupied by elements with related chemical properties. With the exception of Groups 0 and VIII each column contains two subgroups, or families, usually designated as A and B. The elements within a subgroup resemble one another more closely than they resemble the members of the other family subgroup. Thus, in Group I, Li, Na, K, Rb, and Cs are very closely related chemically and constitute family A, whereas Cu, Ag, and Au make up family B, the members of which, although similar to each other, do not bear close resemblance to the elements of family A.

Useful as the modern Mendeleev classification may be in presenting many facts of chemistry in a convenient, concentrated form, it contains many inherent defects. One of the first faults which became evident at an early date was the inversion among certain atomic weights. The periodic law was originally stated by Mendeleev in terms of atomic weights. Later the investigations of Moseley (Sec. 2-7) showed that the properties of the elements are periodic functions of their atomic numbers,

TABLE 3-6 MODERN VERSION OF MENDELEEV'S PERIODIC TABLE

Group Period	0	I	II	III	IV	V	VI	VII	VIII
1		H 1							
2	He 2	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	
3	Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	
4	A 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26
									Co 27
									Ni 28
5	Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44
									Rh 45
									Pd 46
6	Xe 54	Cs 55	Ba 56	La* 57-71	Hf 72	Ta 73	W 74	Re 75	Os 76
									Ir 77
									Pt 78
7	Rn 86	Fr 87	Ra 88	Ac† 89-103	Pb 82	Bi 83	Po 84	At 85	

THE RARE EARTHS

*Lanthanide series	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
†Actinide series	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	En 99	Fm 100	Mv 101	No 102	

and not atomic weights. Moseley's work, therefore, explained the inversions in atomic weights occurring in argon and potassium, in cobalt and nickel, and in tellurium and iodine. Other defects which have not been "ironed out" as satisfactorily are described in the following paragraphs.

The properties of the element hydrogen are so unique that it does not fit into any of the eight groups of Mendeleev's periodic table. Because it exhibits a positive valence toward oxygen of $+1$, hydrogen is frequently placed in Group I, although its nonmetallic properties, and its ability to form a negative ion, would indicate that it might fit just as well, or even better, in Group VII. An unsatisfactory compromise is to place it in both Groups I and VII.

The Mendeleev-periodic table indicates relations that do not necessarily exist. Except for common valences there is usually very little resemblance between the members of the two families in a given group. Certainly there is little chemical similarity between the alkali metals and copper, silver, and gold in Group I. Furthermore even within a family the classification may be somewhat artificial. For example, bivalent copper could fit into family B of Group II, as well as or better than monovalent copper fits into family B of Group I.

Two groups of elements, the lanthanum series of rare earths and the actinium series of radioactive elements, do not fit into the Mendeleev classification. To place either or both of these groups into the body of the table would destroy the effectiveness of the system of classification. For that reason these elements are omitted from the main part of the table and are placed, instead, in separate rows beneath it (Sec. 3·7).

The table places undue emphasis upon one valence of each element, and frequently the valence that is stressed is not the most important one. For instance, copper is indicated by the table as having a valence of 1, which is true; however, copper also has a more frequently occurring valence of 2 that is not indicated by the table.

Other defects of the Mendeleev periodic table may be briefly stated: (1) Three groups of elements, each group consisting of three members, for example, Fe, Co, and Ni, must be placed in Group VIII, although these elements rarely if ever exhibit a valence of 8. (2) No attempt is made to indicate a separation of metals from nonmetals. (3) Despite the fact that chemical properties are directly related to the electronic configuration of various atoms, no satisfactory correlation of this relationship is provided in the table.

3·9 Extended Form of the Periodic Table. The periodic table appearing most frequently in recent textbooks in general chemistry is the extended, or long, form of the table. This extended form, shown in Table 3·7, is sometimes referred to as the *Bohr table*, since it apparently

TABLE 3-7 EXTENDED FORM OF THE PERIODIC TABLE

Group Period	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII	IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
1	H 1														H 1	He 2
2	Li 3	Be 4														
3	Na 11	Mg 12									B 5	C 6	N 7	O 8	F 9	Ne 10
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Pb 82	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac† 89													

THE RARE EARTHS

*Lanthanide series	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
†Actinide series	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	En 99	Fm 100	Mv 101	No 102	

follows the Bohr theory of electronic arrangements for the various types of atoms. However, credit cannot be assigned to any single person for this widely used table. It was first used in a simple form by Rang in 1893, whereas a more complex version was developed by Werner in 1905 and a more modern arrangement was advocated by Bury in 1921. The part played by many others in its development has been summarized by Quam and Quam.¹

This periodic arrangement is obviously an outgrowth of the Mendeleev table and is a noteworthy attempt to overcome some of the latter table's defects. In the extended form of the periodic table the first two periods are broken, in order to place the elements of these short periods in the families to which they clearly belong. In this table the Mendeleev subgroups are eliminated, resulting in the elements falling into 18 columns, corresponding to the periods that contain 18 elements. With this arrangement the transitional elements fall together in the middle portion of the table. It also affords satisfactory positions for Fe, Co, and Ni, and the platinum metals, which in the Mendeleev table were artificially placed in Group VIII. The inert gases, composed of those elements whose atoms have all their electron shells completed, are placed at the end of the periods where they fit more satisfactorily. Many other apparent advantages of the long form over the Mendeleev table have been interpreted.²

The extended form of the periodic table is not without defect. Although it eliminates some of the faults of the Mendeleev chart, many of the latter's defects are retained. The element hydrogen fits no better in this table than in the one developed by Mendeleev. Furthermore no satisfactory positions are provided for the lanthanum and actinium series of elements. It has also been criticized because it fails to reflect the electronic configuration of the various elements.³

3.10 A Periodic Table Based upon Electronic Configurations. Attempts to overcome the admitted defects of the Mendeleev classification of the elements have led to a wide assortment of charts. Among the better two-dimensional arrangements of the elements that have endeavored to distinguish the various elements by indicating the outer electronic structure of their atoms is one developed by Gardner⁴ in 1930. This arrangement, modernized by Luder⁵ and improved by Babor,⁶ is given in Table 3-8. The chart contains 32 columns and divides the elements into

¹ G. N. Quam and M. B. Quam, *J. Chem. Educ.*, **11**: 217 (1934).

² L. S. Foster, *J. Chem. Educ.*, **16**: 409 (1939).

³ W. F. Luder, *J. Chem. Educ.*, **20**: 21 (1943).

⁴ R. Gardner, *Nature*, **125**: 146 (1930).

⁵ Luder, *loc. cit.*, **20**: 21 (1943).

⁶ J. A. Babor, *J. Chem. Educ.*, **21**: 25 (1944).

TABLE 3-8 THE PERIODIC TABLE BASED ON ELECTRON CONFIGURATION

Period	The representative elements																		The related or transitional metals										The lanthanum and actinium series of elements											
	Differentiating electron in highest energy level or shell																		Differentiating electron in second highest energy level or shell										Differentiating electron in third highest energy level or shell											
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32								
1	H	He																																						
2	Li	Be	B	C	N	O	F	Ne																																
3	Na	Mg	Al	Si	P	S	Cl	A																																
4	K	Ca							Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn																						
5	Rb	Sr							Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd																						
6	Cs	Ba							La																															
7	Fr	Ra							Ac																															

three major classifications, which have been designated as *representative elements*, the *related or transitional elements*, and the *lanthanum and actinium series of elements*. It is similar to the Mendeleev and the extended tables in that it contains seven periods arranged horizontally.

It will be noticed that the classification of the elements on this chart follows closely the *types of elements* listed in Sec. 3-7. The position of a given element is determined by the number of electron shells, the number of incomplete shells, and the quantum number of the electron which differentiates the atom of the element from its neighboring elements. The quantum number of the differentiating electron also serves to classify the element into one of the three major classifications.

The Gardner-Luder-Babor classification of the elements is an arrangement which emphasizes the differences in electron configurations among the atoms in preference to a periodic arrangement in the order of atomic numbers. In spite of the attractiveness of this chart for teachers and graduate students it has been expanded to such a degree that it is no longer a periodic table. Later we shall deal with a large topic entitled the Periodic Functions of the Elements, and in this study it will become clear that one of the essential purposes of a periodic table is to indicate, to a student, the reoccurring properties among the elements. The Gardner-Luder-Babor table is inadequate for this purpose.

3-11 A Periodic Table Indicating the Relative Sizes of Atoms and Ions. One of the most interesting of recent periodic charts is one devised by Campbell,¹ which is nothing more than the extended form of the periodic table, in which the atoms and their ions are indicated as circles of varying sizes. The radii of these circles show the relative size of these particles as calculated from X-ray data. As is explained in Secs. 3-15 and 3-17, there is a close relationship between the size of atoms or ions and their physical and chemical properties. Although other periodic tables have been used to indicate the relative size of atoms and the relative size of ions, this ingenious table is the first of its kind to indicate the periodicity of these dimensions in combination with the extended form of the periodic table. The structure of the Campbell arrangement is given in Fig. 3-2, and it may be safely predicted that this chart will become increasingly important as an effective teaching aid in general chemistry.

✓ PERIODIC FUNCTIONS OF THE ELEMENTS

Many types of periodic tables have been developed for the purpose of classifying the elements into groups with somewhat similar properties. The development of these tables resulted in the formulation of the *periodic law*, which was originally stated as follows: *The properties of the*

¹ J. A. Campbell, *J. Chem. Educ.*, **23**: 525 (1946).

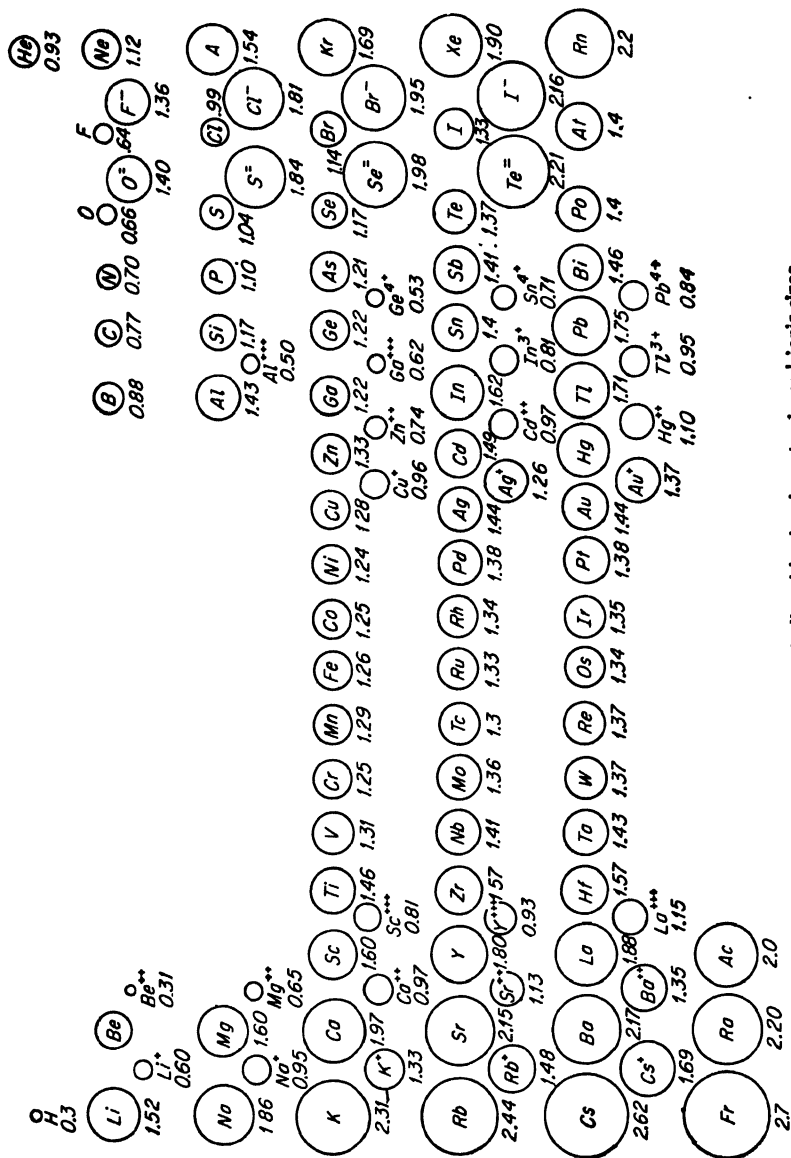


Fig. 3.2 The Campbell periodic table showing atomic and ionic sizes.

elements are periodic functions of their atomic weights. We now know that this is a somewhat inexact statement, inasmuch as atomic weight is a nuclear property and not directly related to the electronic structure of an atom. From the results of Moseley's investigations (Sec. 2-6) it is now recognized that the chemical and most of the physical properties depend on the number and arrangement of the extranuclear electrons, rather than on the atomic weight. However, there is a fairly close relation between mass number and atomic number (Sec. 1-12), and, during the latter part of the nineteenth century, the original statement of the periodic law was sufficiently accurate to serve as an invaluable aid in smoothing out certain imperfections in the classification of the known elements and as a prophetic guide in predicting the properties of those elements to be discovered.

The designation *periodic* in most of the classifications of the elements serves to indicate that certain characteristic properties reappear at definite intervals. Thus, when the elements are arranged in the order of their atomic numbers, there appears a periodicity, not only in their chemical properties, but also in their physical properties and in their electronic structures.

Two structural properties, the size and the ease with which electrons may be removed, largely determine the chemical behavior of the atoms. Moreover the close relationship between these two fundamental properties prevents the discussion of the effect of one of these properties upon chemical behavior without including the other.

3-12 Density. The densities of the elements in the solid state vary periodically with their atomic numbers, as is shown in Table 3-9. The

TABLE 3-9 THE DENSITIES OF THE ELEMENTS OF THE SECOND AND THIRD PERIODS

Na 0.97	Mg 1 74	Al 2 74	Si 2 42	P 2 20	S 2.07	Cl*			
K 0.87	Ca 1 54	Sc 2 5	Ti 4 5	V 5 96	Cr 6 92	Mn 7 42	Fe 7.8	Co 8.9	Ni 8.9
	Cu 8 93	Zn 7.15	Ga 5.91	Ge 5.47	As 5.73	Se 4 8	Br*		

* Densities in the liquid state.

periodicity varies in a regular manner from member to member within a period and reaches a maximum in the central members. The change in density with atomic number for the lighter elements is indicated graphically in Fig. 3-3.

3-13 Melting Point. Another periodic property of the elements is indicated graphically in Fig. 3-4, in which the melting points of the

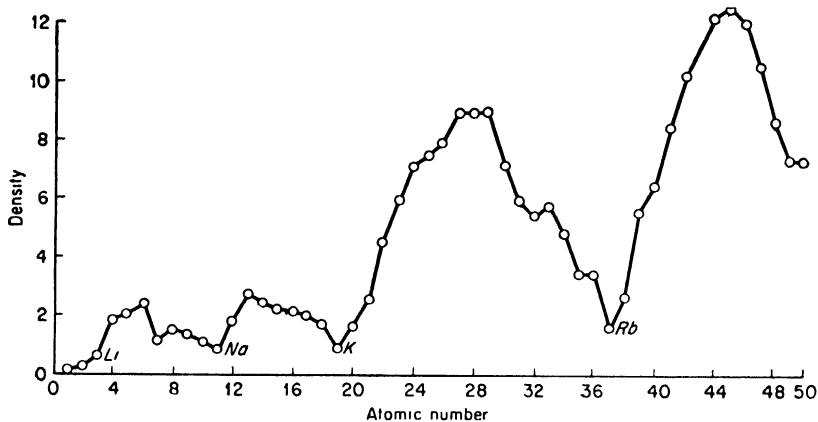


Fig. 3-3 Periodicity of density for elements 1 to 50.

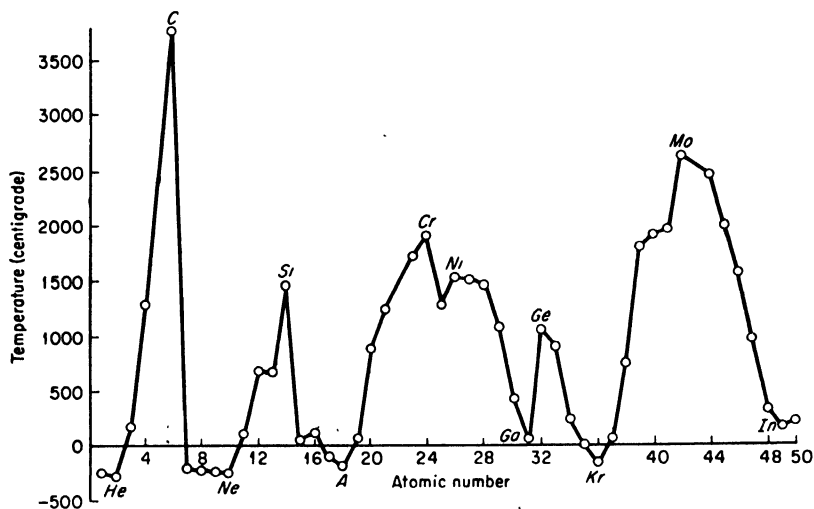


Fig. 3-4 Periodicity of melting points for those elements with atomic numbers 1 to 50.

lighter elements are plotted against their atomic numbers. From this plot it may be observed that melting point occurs as a minimum (or near minimum in the case of neon) in the inert gases and as a maximum in Group IV (for the lighter elements) and Group VI (for the heavier elements). Also it may be noted that members of the same family of elements occupy similar positions on the ascending or descending portions of the curve.

3-14 Atomic Volume. In Sec. 3-4 it was stated that Lothar Meyer apparently arrived at his classification of the elements through an analysis of certain relationships which were based upon physical properties. Moreover we are indebted to Meyer for many curves which represent graphically certain physical periodicities. Of these graphical representations the most famous is his atomic-volume curve, in which he sought to relate the mass of the atoms to their atomic volumes. This he showed by

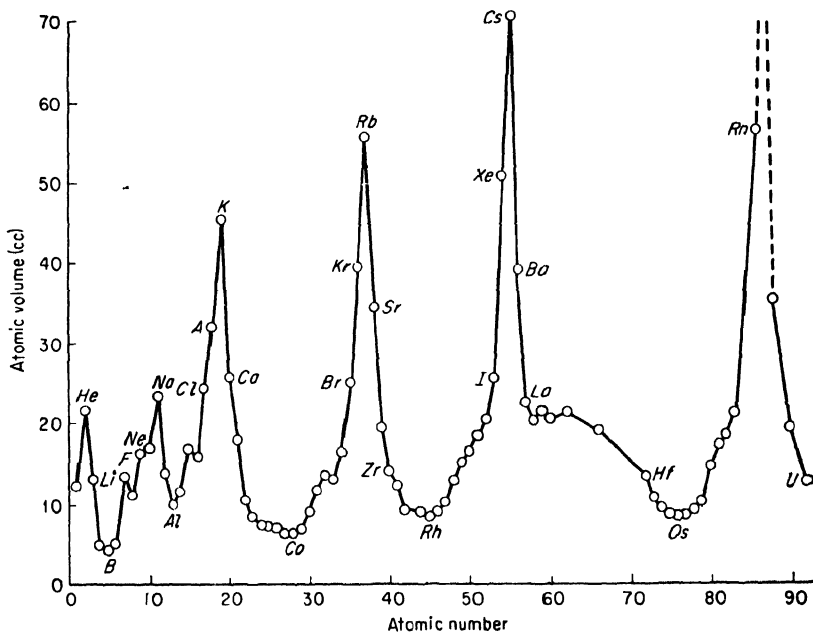


Fig. 3-5 The atomic volumes of the elements.

plotting atomic volume against atomic weight. The resulting curve takes the form of a series of well-defined loops, upon which similar elements are found occupying analogous positions. It is of interest that the ascending slopes of these loops contain the electronegative elements and the descending slopes the electropositive ones, whereas the alkali metals occupy the maximum positions on the curve. A modern version of Lothar Meyer's curve is given in Fig. 3-5. In the more modern interpretation atomic number is substituted for atomic weight.

Atomic volume is defined as the volume occupied by 1 gram atom of an element; mathematically, it is the atomic weight divided by the density. According to this definition the atomic volume is the volume of 1 gram atom; by Avogadro's hypothesis, it is the volume occupied by 6.023×10^{23} atoms of an element. Therefore the atomic volumes of the elements

should be the volumes occupied by the same number of atoms. However, the latter conclusion is somewhat erroneous because of certain variable factors, which, for the most part, are connected with the way atoms are packed in various elements. Among the conditions that may affect the reliability of the atomic volume curve are the following:

1. Many elements exist in more than one allotropic form, and the densities of the allotropes differ considerably. For instance, the densities of diamond and graphite are 3.52 and 2.25, respectively, and the former falls very low on the atomic-volume curve, whereas the latter, with a greater atomic volume, falls into its normal position upon the graph. However, the selection of graphite as the standard is quite arbitrary. In many cases it is impossible to justify the choice of one allotrope over another.

2. No very reliable comparison can be made between the atomic volumes of elements existing in different physical states. Thus it is impossible to compare the atomic volume of an element in the gaseous state with one in the solid state. For those cases in which densities in the solid state are not reliably known, it is necessary to compromise and use densities in the liquid state. Even so, a comparison between the atomic volume of elements such as liquid oxygen and solid sodium is more or less meaningless because of the wide differences in the amount of free space between atoms or molecules.

3. Any reliable comparison between the atomic volumes of two or more elements must be made from values obtained at corresponding temperatures. This necessity arises as a result of the change in density with temperature. Theoretically the most favorable temperature for such a comparison is absolute zero, but for experimental reasons it is impossible to determine the densities of the elements at this temperature. Furthermore it is unfortunate that insufficient data are available at other temperatures which might be used for correlations, such as the freezing points and boiling points.

4. The various elements have several different types of crystal lattices, and the distance between atoms or molecules in a lattice depends upon the packing arrangement. Consequently, unless elements possess identical lattices, there will be an error in comparing their atomic volumes.

5. Molecules among the elements contain a varying number of atoms. For instance, the molecules of a metal are monoatomic, whereas the molecules of most common gases are diatomic. In the case of rhombic sulfur, which is a solid, there are apparently eight atoms in each molecule. However, in the latter case, there is no justification for the assumption that the atomic-volume of sulfur is equal to one-eighth of its molecular volume. Despite the many factors which indicate the unreliable basis upon which the atomic volume curve is constructed, it is nevertheless

surprisingly regular in its representation of the periodicity of atomic volume as well as other properties in the elements.

Of interest is the position of the rare earths (lanthanons) on the atomic-volume curve. Beginning with lanthanum, these elements are unusual in that they are formed by a progressive increase in mass and charge upon the nuclei; yet the differentiating electrons go, not into the valence shell, but into the third from the outermost shell. Since the volume of an atom is determined by the distance from the nucleus of the outer quantum group, this form of atom building becomes significant. In the rare earths the increasing atomic number (charge on the nucleus) causes the valence electrons to become more and more firmly held, despite the screening effect of the added electrons. Furthermore, as the attractive force of the nucleus for the valence electrons becomes progressively larger, each successive lanthanon contracts in size. This shrinkage is known as the lanthanide contraction. Hence the rare earths show diminishing atomic volumes with increasing atomic numbers, as evidenced in Fig. 3-5. Moreover the effect of the lanthanide contraction continues in those elements immediately succeeding the lanthanons. This accounts for the fact that the expected periodic increase in atomic volume for elements beginning with hafnium does not appear. The effect of the lanthanide contraction upon post-lanthanon elements also explains the existence of pairs of elements, located on the atomic-volume curve before and after the lanthanons, which have almost identical volumes and the same number of valency electrons. As might be expected, these pairs of elements are remarkably similar in their chemical properties. Thus the lanthanide contraction can be held responsible for the close chemical similarity of the post-lanthanon elements hafnium, tantalum, and tungsten to the corresponding pre-lanthanon elements zirconium, niobium, and molybdenum.

3-15 Other Physical Properties. Almost any physical property of the elements, if plotted against the atomic numbers, will show a periodicity, and usually the curve so obtained closely parallels the atomic-volume curve. Among these periodic properties which have not already been discussed are hardness, malleability, compressibility, coefficient of expansion; thermal conductivity, and electrical resistance. Likewise, the physical properties of analogous compounds of the elements, such as melting point, boiling point, stability, color, and solubility, are often periodic. However, of most importance to the chemist is the fact that these periodic similarities occurring among the elements and their compounds have greatly simplified the task of organizing the extensive mass of knowledge relating to inorganic materials.

Not only do the physical properties of the elements and their compounds show periodic changes within the limits of each series, but there is

144 Fundamental Concepts of Inorganic Chemistry

also a gradation of properties within a given group or family. In other words, although the properties of the first element in a family reappear in other elements within the family, there is also a more or less regular change in these similar properties in passing from the lowest to the highest member in the group. For instance, the boiling points of the inert gases increase as the atomic number increases. Furthermore the gradation in properties frequently follows the course indicated in the atomic-volume curve, since this curve is fairly representative of the periodicity of most physical properties. This gradation within groups is illustrated more emphatically by the data presented in Table 3-10.

TABLE 3 10 GRADATION OF PHYSICAL PROPERTIES OF ELEMENTS
WITHIN GROUPS

Boiling points of the inert gases, °C	Specific heats of the alkali metals, cal/g	Densities of Group IV ele- ments, g/cc	Melting points of the halogen elements, °C
He -268.9	Li 0.837	C 2.25	F -223
Ne -245.9	Na 0.297	Si 2.42	Cl -101.6
A -185.7	K 0.192	Ge 5.35	Br -7.3
Kr -152.9	Rb 0.079	Sn 7.28	I 113.6
Xe -140.0	Cs 0.018	Pb 11.34	At ?
Rn -71	Fr ?		

3-16 (Atomic Radii. The term *radius* for an atom or ion is usually considered as the distance from the center of the nucleus to the outer shell of the atomic particle. It is obviously impossible to isolate an individual atom or ion and determine its radius, especially since its size or radius is affected by the association with other particles.

According to J. A. Campbell¹ atomic radii in compounds depend largely on: (1) the multiplicity of the bond, i.e., whether the bond is single, double, or triple; (2) the oxidation number of the atoms, which indicates the number of electrons involved in the bonding; (3) the extent to which the bonding is ionic or covalent, i.e., the percentage ratio of the bond types; (4) the coordination number of the atoms; and (5) the repulsive forces between atoms not directly bonded. As might be expected from these five variable factors, the atomic radius of an atom of a particular element may differ from one substance to another. Some of the variations produce relatively little effect on the apparent atomic radii, and fortunately all the factors are so interrelated that it is possible to use only the first two as criteria in the calculations of the relative sizes of atoms.

X-ray investigations of crystals have furnished data for assessing the radii of various elements, in both their ionic and their atomic form. In

¹ *Ibid.*

using these data it has been necessary to assume that an atom or ion behaves as an effective sphere which is barely in contact with another atom or ion in the crystal. Thus the distance between the centers of two adjacent atoms or ions is equal to the sum of their characteristic radii, or, in other words, the radius of the atom or ion is one-half of the single-bond distance between the nuclear centers of the two particles. X-ray measurements have been made on a number of crystals in which the binding is known to be covalent and the atomic distances obtained. The values for a few atoms, such as carbon and sulfur, whose crystal structures are known, have served as starting points for the measurements and calculations of other atomic radii. For example, the single-bond distance between carbon to carbon has been measured in diamond as 1.54 Å, and in normal and cyclic hydrocarbons, which contain series of CH_2 groups linked together, the distance has been found to vary between 1.52 and 1.55 Å. This constancy of bond length indicates that any appreciable deviation from 1.54 Å for a carbon-to-carbon linkage must result from a different arrangement of electron sharing. Moreover, if it is assumed that the carbon atoms are spheres barely in contact with each other, the atomic radius of the carbon atom is one-half of the carbon-to-carbon bond, or 0.77 Å. To continue our illustration, the single-bond distance between atoms in pure silicon has been measured as 2.34 Å, and it may be assumed that the radius of the silicon atom is 1.17 Å. The arithmetical sum of the values for the radii of the carbon and silicon atoms is 1.94 Å, indicating that the C-Si bond distance in silicon carbide is of this value. Conversely it is possible to assign to the elements values for covalent radii, the sums of which give the length of the covalent bonds between adjacent atoms in various substances. Thus, if the C-F single-bond distance is measured as 1.41 Å, it may be deduced that the atomic radius of the fluorine atom is 0.64 Å by subtracting the value of the atomic radius of carbon from the bond distance. \

It must be admitted that the foregoing explanation of the methods used in assigning values for the atomic radii of the various elements is an oversimplification of the true procedures. As has been stated in an earlier paragraph, atomic radii are affected by a number of variables, and where possible these effects must be taken into consideration in calculating the size of atomic particles. Frequently the term *single bond* is qualified by a descriptive word or phrase to indicate a variation which may change the bond length. This is exemplified by the *tetrahedral* bond, which describes a bond as being one of four covalent bonds attached to an atom in an sp^3 bonding (Sec. 4.14). The tetrahedral radius may vary slightly from a *normal* radius, the latter being a term to denote the atomic radius for an element exhibiting its normal valence but in which the coordination number is less than 4. Hence the atomic radius of an atom may have a

146 Fundamental Concepts of Inorganic Chemistry

number of slightly varying values depending upon whether the bonding is normal, tetrahedral, square, or octahedral. Other radii are designated as *metallic*, indicating the bonding of atoms occurring in metals. This term is necessary for describing radii for those active metals which do not form covalent compounds. Fortunately metallic and covalent radii are so closely related that the terms and values may be used interchangeably. Furthermore it is generally agreed that the sizes of free atoms and those values obtained for the same atoms occurring in covalent compounds are

TABLE 3-11 TETRAHEDRAL ATOMIC RADII

Be 1.07 (1.11)	B 0.89	C 0.77	N 0.70	O 0.66	F 0.64
Mg 1.40 (1.60)	Al 1.26 (1.43)	Si 1.17	P 1.10	S 1.04	Cl 0.99
Cu 1.35 (1.28)	Zn 1.31 (1.33)	Ga 1.26 (1.22)	Ge 1.22	As 1.18 (1.21)	Se 1.14 (1.17)
Ag 1.53 (1.44)	Cd 1.48	In 1.44 (1.62)	Sn 1.40	Sb 1.36 (1.41)	Te 1.32 (1.37)
Au 1.50 (1.44)	Hg 1.48 (1.55)	Tl 1.47 (1.71)	Pb 1.46 (1.75)	Bi 1.46 (1.51)	I 1.28 (1.33)

apparently the same. Therefore, from the subsequent discussion, it may be rightfully inferred that it is usually possible to use the terms *atomic radius*, *covalent radius*, *normal radius*, and *tetrahedral radius* synonymously, since such use rarely involves an appreciable error.

Values of the tetrahedral covalent radii¹ for many of the common elements are given in Table 3-11. These values were derived from interatomic distances in crystals in which the atoms form four sp^3 tetrahedral bonds. In those elements where the normal radii differ from the tetrahedral, the former are shown in parentheses.

In the previous section it was suggested that almost any physical property of the elements is a periodic function of their atomic numbers. This implication may be extended to include the size of atoms of the elements. Although the periodicity in relation to size among the elements is not so

¹ Linus Pauling and M. L. Huggins, *Z. Krist.*, **87**: 205 (1934).

pronounced as the periodicities for some other physical properties, it is nevertheless present. A comparison of Table 3-11 with a modern version of Mendeleev's periodic table of the elements discloses two periodic regularities in connection with atomic size. First of all, there is a progressive decrease in size along each series (or row) from left to right as the atomic number increases. For example, the first member of the second series listed in Table 3-11 is magnesium with an atomic radius of 1.40 Å, and the sizes of the atoms in this series decrease progressively through chlorine, which has an atomic radius of 0.99 Å. This general decrease in size is due to a corresponding increase in the atomic number for the elements concerned. Since atomic number denotes the magnitude of the positive charge on the nucleus, it is evident that, as this charge increases, the electrons are attracted more strongly to the nucleus, resulting in a decrease in atomic size. This decrease in size has a pronounced influence on the metallic properties of the atoms. As a general rule, the larger the atom, the farther from the nucleus are the valence electrons, and, consequently, the more metallic is the atom. It might also be stated that, if two atoms have approximately the same size, the one with the larger atomic number (greater nuclear charge) is less metallic. In other words, nonmetallic elements are those with small atoms and large nuclear charge. Returning to our original statement in regard to the progressive decrease in size within a given series with increasing atomic number, it should also be pointed out that this decrease is less pronounced as the atomic weight increases. To illustrate this statement with values from Table 3-11, the difference in size between magnesium and chlorine in the second series is greater than that between cadmium and iodine in the fifth series.

The second periodic regularity, in relation to atomic size, occurs within a given family (or column) of the elements. This periodicity is manifested as a tendency on the part of the elements in any one family to increase in size as the atomic number increases. The number of electrons in the valence layer of the elements in a given family remain constant, but the total number of electron layers increase with atomic number, and this latter augmentation causes a progressive expansion in size as the atomic number becomes larger. However, the increment in size within a family is less pronounced as the atomic number becomes greater. These statements may be verified from values in Table 3-11; for example, there is a large increase in size in going from beryllium, with an atomic radius of 1.07 Å, to magnesium, with a radius of 1.40, whereas there is no difference in the radii of cadmium and mercury in the lower part of the same family. At this point it seems pertinent to restate the fact that the metallic properties of large atoms are more pronounced than those of small atoms. Again, we may use Table 3-11 to illustrate our

point by calling attention to the difference in metallic properties between the relatively small atoms in the upper series and the larger atoms in the lower series. The latter are decidedly more metallic in nature.

3-17 Valency. Periodicity in valence among the elements was first recognized by Mendeleev. In fact he pointed out that the number of a group corresponds with the valency of the elements in it. The valence of an element, commonly referred to as *valence number*, or *oxidation number*, was originally defined as the combining capacity of an element

TABLE 3-12 ABEGG'S CONCEPTION OF VALENCY OF THE ELEMENTS

	Na	Mg	Al	Si	P	S	Cl
Normal valences.....	+1	+2	+3	+4	-3	-2	-1
Contravalences.....	-7	-6	-5	-4	+5	+6	+7

and, in terms of the original definition, is equal to the number of atoms of hydrogen that an element will combine with or replace. A more frequently used term than valence is that of oxidation number, which may be defined as the number of electrons lost or gained by an atom as the result of combining with other atoms to form an ionic compound, or the number of electrons shared by an atom with other atoms in the formation of a covalent compound.

TABLE 3-13 PERIODICITY OF THE ELEMENTS WITH RESPECT TO VALENCY

	Groups						
	I	II	III	IV	V	VI	VII
Series 1	LiCl Li ₂ O	BeCl ₂ BeO	BCl ₃ B ₂ O ₃	CCl ₄ ; CH ₄ CO ₂	NH ₃ N ₂ O ₅	H ₂ O	HF
Series 2.....	NaCl Na ₂ O	MgCl ₂ MgO	AlCl ₃ Al ₂ O ₃	SiCl ₄ ; SiH ₄ SiO ₂	PH ₃ P ₂ O ₅	H ₂ S SO ₃	HCl Cl ₂ O ₇

As early as 1904 Abegg stated that every element possessed a maximum valency of 8, this number being made up of positive and negative components, sometimes designated as normal valences and contravalences. The first series of the periodic table of the elements is used in Table 3-12 to illustrate Abegg's idea of valency. From Abegg's conception of valency was developed the rule of eight and the octet theory, both of which refer to the erroneous idea, once widely believed, that all atoms enter into chemical combination to attain an outermost structure containing eight electrons. These ideas will be discussed more completely in Chap. 4.

The periodicity in chemical nature of the first two series of the periodic

table toward chlorine and hydrogen follows Abegg's conception of normal valency. Toward oxygen, however, the elements exhibit a valence ascending from 1 through 7. Periodicity of valency is illustrated by the different valences exhibited by elements in the various compounds listed in Table 3-13. Using the compounds given in Table 3-13 as criteria, it can be stated that in progressing from left to right in the periodic classification, along any series of typical elements, the hydrogen valency increases from 1 to 4 and then decreases again to 1, whereas the oxygen valency increases from 1 to 7.

2-18 Ionic Radii. The radii of atoms are altered by the addition or loss of electrons. Since the charge on the nucleus remains the same during these alterations, the change in size resulting from an atom being

TABLE 3-14 DECREASE IN SIZE OF ATOMS IN PRODUCING VARIOUS CATIONS

Element Atomic radius, A	Fe 1 26	Mn 1.29	Pb 1.75
Ion Ionic radius, A	Fe ⁺⁺ 0 75	Mn ⁺⁺ 0 80	Pb ⁺⁺ 1.21
Ion Ionic radius, A	Fe ⁺⁺ 0 60	Mn ⁺⁺ 0.52	Pb ⁺⁺ 0 84

converted into an ion can be attributed either directly or indirectly to the change in number of electrons. When an atom loses electrons, a positive ion is formed, which is appreciably smaller than the neutral atom. This smaller size is due to a concentration of the attractive force of the nucleus upon a smaller number of electrons, holding them more tightly, and causing a contraction in the volume occupied by the remaining particles. On the other hand, when a negative ion is formed, the opposite process takes place. In this case the electrostatic force exerted by the nucleus is distributed over a greater number of electrons than were present in the neutral atom; consequently there is an expansion in volume to accommodate the increased number of negative charges. Hence it is possible to frame a general rule to the effect that the ionic radius of any cation is smaller than the radius of the neutral atom, whereas the radius of the anion is always greater. Furthermore, if an element exhibits more than one positive valence, i.e., if different numbers of electrons can be stripped from the atom to form more than one ion, then the radius decreases progressively with loss of electrons. The change in size of atoms with successive losses of electrons is illustrated in Table 3-14.

If two oppositely charged ions are brought together, they are attracted to each other by electrostatic attraction as predicted by Coulomb's law of electrostatic force; however, as they approach close to one another, the

attractive force is counteracted by a repulsive force produced by the two electronic systems. At some point, or interionic distance, the two opposing forces will just balance each other, and this might be called the *equilibrium distance*. The electrostatic force exerted by an ion is not spatially directed; consequently the radius of any given ion is not constant but varies with the number of unlike charges around it. By X-ray methods

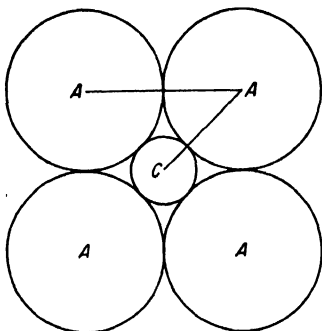


Fig. 3-6 Method for the calculation of ionic radii from interatomic distances in crystals with the sodium chloride structure.

it is possible to determine distances between the centers of two oppositely charged ions, and since such ions are packed in crystals as if they were spheres of characteristic sizes, it is also possible to assign "ionic radii" to the ions. The ionic radii so assigned are not actual radii, but instead represent the effective or apparent radii of the ions packed within a crystal. In other words, the apparent ionic radii of two oppositely charged ions are values so chosen that the sum of the two radii will be equal to the equilibrium distance between the two ions in contact with each other within the crystal. Ionic distances, therefore,

are always fractions of interionic distances so chosen that they may be used to predict other interionic distances in other crystals.

The coordination number of an ion in the majority of ionic crystals is determined by the number of surrounding ions of opposite charge; i.e., the sodium ion is surrounded by six chloride ions in the sodium chloride lattice. By means of X-ray measurements the distance between the sodium ion and the chloride ion can be measured, but it is impossible to decide what part of this distance should be assigned as the radius of the sodium ion and what part for the chloride ion. Fortunately many positive ions are small as compared with the negative ions packed around them.¹ Thus, in Fig. 3-6, the small central cation may be represented as *C* with four large anions designated as *A* packed around it. If it is assumed that the anions are in contact with one another, then the radius of one anion is half the distance between two anions. Furthermore the radius of the cation may be deduced by subtracting the radius of the anion from the interionic distance between the oppositely charged ions. By this method of analysis many oxides show a minimum distance between oxygen centers of about 2.7 Å. In 1923 J. A. Wasastjerna¹ calculated the ionic radii of O^{2-} and F^{-} ions to be 1.32 and 1.33 Å, respec-

¹ J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, 1 (38): (1923).

tively. Using these values as standards, V. M. Goldschmidt¹ has worked out a fairly complete set of ionic radii by substitutional methods from measured interionic distances. Some of his values are given in Table 3-15.

Pauling² has derived a theoretical set of radii based on the general idea that the radii of ions with the same electronic configuration, such as Na^+ and F^- , are inversely proportional to the effective charges on the ions. The effective nuclear charge is assumed to determine the distribution of the outer electrons and, consequently, the size of the ion.¹ It is defined

TABLE 3 15 RADII ANGSTROMS, OF IONS WITH INERT GAS CONFIGURATIONS

	H^- 1 54	Li^+ 0 60	Be^{++} 0 31	B^{++} 0 20	C^{++} 0 15	N^{++} 0 11	O^{++} 0 09	F^{++} 0 07
O^- 1 40	F^- 1 36	Na^+ 0 95	Mg^{++} 0 65	Al^{++} 0 50	Si^{++} 0 41	P^{++} 0 34	S^{++} 0 29	Cl^{++} 0 26
S^- 1 84	Cl^- 1 81	K^+ 1 33	Ca^{++} 0 99	Sc^{++} 0.81	Ti^{++} 0 68	V^{++} 0 59	Cr^{++} 0 52	Mn^{++} 0 46
Se^- 1 98	Br^- 1 95	Rb^+ 1.48	Sr^{++} 1 13	Y^{++} 0 93	Zr^{++} 0.80	Nb^{++} 0 70	Mo^{++} 0 62	Tc^{++}
Te^- 2.21	I^- 2 16	Cs^+ 1 69	Ba^{++} 1 35	La^{++} 1 15	Hf^{++} 0 79	Ta^{++} 0 71	W^{++} 0 65	Re^{++} 0.50

as the actual nuclear charge Ze minus the screening effect Se of the remaining electrons in the ion. The screening factor is deduced experimentally from spectral data. Thus the screening factor S for ions with the neon structure is interpreted as a value of 4.52; therefore the effective nuclear charges of the Na^+ and F^- ions are their actual nuclear charges less 4.52, or $6.48e$ and $4.48e$, respectively. If the interionic distance 2.31 Å between these two ions is apportioned in the inverse ratio of the effective nuclear charges, the values so obtained are 0.95 Å for the radius of the sodium ion and 1.36 Å for the fluorine ion. In a similar manner Pauling has evaluated the radii of the alkali and halogen ions. These values have been used to obtain the radii of other ions with the same number of electrons, but with different effective charges, by assuming that the electron atmosphere (volume of the ion) is inversely proportional to the effective charge.¹ Some of the values calculated by Pauling are given in Table 3-15.

From the foregoing explanations as to the methods for estimating ionic

¹ V. M. Goldschmidt, *Trans. Faraday Soc.*, **25**: 253 (1929).

² L. Pauling, *J. Am. Chem. Soc.*, **49**: 765 (1927).

radii it is obvious that the magnitudes of individual radii are dependent upon the method used to apportion observed interionic distances between the ions involved in the measurements. This also accounts for the variance among these values as listed in the chemical literature; however, these differences are usually no more than a few hundredths of an angstrom, which represent no real significance. We are particularly interested in the change of ionic radii with atomic number, and values obtained by almost any method show a definite periodicity. /

In Table 3·15 are listed values of ionic radii for some ions with inert gas configurations. It should be pointed out that those ions indicated as bearing high positive charges, on the right side of the table, do not exist as simple ions. These values simply represent magnitudes for the particular ions in coordination compounds. A comparison of this table with a modern version of Mendeleev's periodic classification of the elements indicates the same periodic regularities in relation to size, except they are more pronounced, as was disclosed in Sec. 3·16 in regard to atomic radii. Thus, in going from left to right along any series, there is a pronounced and progressive decrease in ionic radii. This decrease is to be expected since the attraction of the nucleus for remaining electrons increases with the number of electrons lost. The other periodicity, similar to that among atomic radii, is manifested as an increase in size in passing from the top to the bottom of the table among any one family. The increase may be attributed to the added electron layers in progressing from one element to another within any particular family. It should also be noted that in any series of isoelectronic ions, i.e., ions with the same configuration of orbital electrons, the radii decrease rapidly with decreasing positive charge. This decrease may be illustrated in the fluoride, sodium, magnesium, and aluminum ions, where the over-all change in radius is from 1.36 Å in the fluoride ion to 0.50 Å in the aluminum ion.

The size of an ion is obviously a physical property, but this property is so closely interlinked with chemical behavior that any discussion of one must include some mention of the other. An analysis of the various forces which may operate between atoms and ions will be presented in Chaps. 4 and 5, but it seems pertinent to mention at this point that the so-called "chemical linkages" are frequently dependent upon, or related to, size. Thus, as we shall learn later (Secs. 5·4 and 5·5), the extent of hydration of cations in aqueous solutions and the consequent acidities of such solutions are directly related to the radii of the ions involved. Furthermore, according to Fajan's rules (Sec. 4·4), the tendency to form ionic or covalent linkages is related to the deformability of the electron shells of the reacting ions; and the extent of the deformation that may be produced is directly dependent upon the radii of the cation and anion which are in contact.

3.19 Ionization Potentials. Probably the most fundamental property of an atom that we are able to measure is its *ionization potential*. The term, more properly called the *first ionization potential*, is defined as the work necessary to remove the most loosely held electron from a normal atom, leaving it positively charged. The amount of energy required to perform this work may be evaluated either in kilocalories or in electron volts, the latter unit being the one most frequently used. A curve showing the periodic variations of the first ionization potentials with atomic

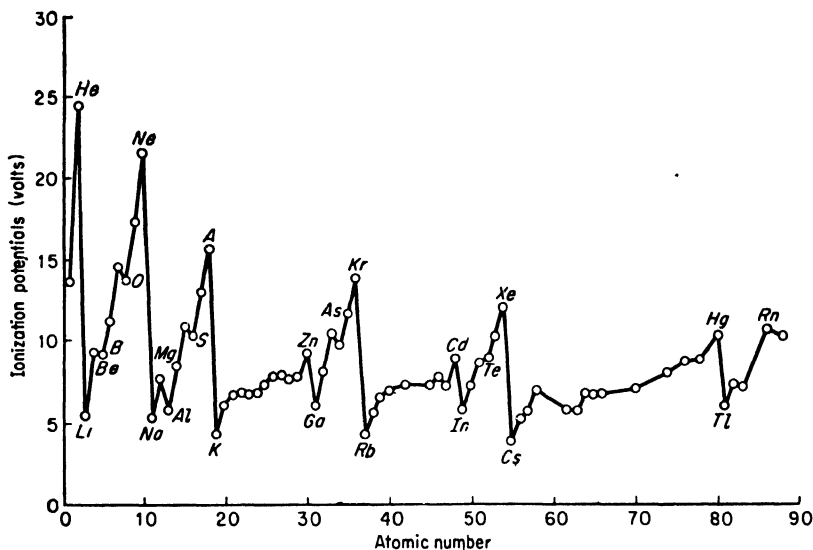


Fig. 3.7 The first ionization potentials of the elements.

numbers, for the different elements, is given in Fig. 3.7. The periodicity which is indicated in this curve is quite pronounced and corresponds identically with the periods of the Mendeleev table. Consequently the atomic numbers of those elements occurring at the peaks of the curve are the inert gases, which are also the elements at the end of each period in Mendeleev's classification.

The first ionization potential is measured for the outermost electron or electrons, whereas each row in the periodic table is made up of elements in the order in which their outermost shells are filled with electrons. In progressing along any row the ionization potentials tend to increase from left to right. This tendency may be attributed to a rising nuclear charge as the atomic number is increased, and is culminated at the end of each row. Furthermore, in the building up of any particular row, there is a slight decrease in the radii of the atoms involved. These two factors, the

154 Fundamental Concepts of Inorganic Chemistry

increase in nuclear charge and the decrease in radius, operate to bind each added electron more tightly to the nucleus. Still other factors are involved in holding the outer electrons to an atom, but, before continuing with them, our explanation up to the present may become clearer by examining Table 3-16, in which certain related periodicities for the first row of the periodic table are tabulated.

TABLE 3-16 SOME RELATED PERIODICITIES IN THE FIRST ROW OF THE PERIODIC TABLE

	Elements							
	Li	Be	B	C	N	O	F	Ne
Nuclear charge.....	3	4	5	6	7	8	9	10
Number of outermost electrons.....	1	2	3	4	5	6	7	8
Radius, Å.....	1.52	1.07	0.89	0.77	0.70	0.66	0.64	1.12
First ionization potential.....	5.39	9.32	8.30	11.26	14.54	13.64	17.42	21.56

If we retain the Bohr conception of the atom, it is possible to describe at least four factors which affect the magnitude of ionization potentials: These influences may be designated as: (1) the size of the nuclear charge; (2) the atomic radius; (3) the screening effect of inner electron shells; and (4) the ellipticity of the electron's orbit. All these various aspects are related to atomic structure and were described at some length in Chap. 2; therefore the present discussion will avoid repetition of this material as much as possible.

According to Coulomb's law the force operating between two electric charges is directly proportional to the product of their magnitudes and inversely proportional to the square of the distance between them. However, within the atom various disturbing influences prevent more than approximate adherence to the law of electrostatic attraction. In fact the law serves only as a rough prediction of the effect of the first two factors, listed in the preceding paragraph, upon the size of the ionization potentials. The first ionization potential, as indicated by Fig. 3-7 and in Table 3-16, increases somewhat irregularly in progressing along a row in the periodic table. The irregular increase must be attributed to disturbances resulting from the other factors just mentioned.

The periodicity among ionization potentials is produced by the sudden increase in average distance between the nucleus and the beginning of a new shell. At the same time there is a corresponding decrease in the effective nuclear charge due to the shielding effect of the electrons in the inner shells. If electrons are arranged in shells about the nucleus of an atom, it may be assumed that an inner shell acts as a screen, or shield, to

decrease the attractive force of the positively charged nucleus for an electron or electrons beyond the shell. Therefore each inner shell existing between the nucleus and the outermost shell produces a shielding effect which weakens the force holding the outer electrons to the atom. Furthermore it is believed that the screening effect is related to the magnitude of the electric charges involved and is an inverse function of the distance between the screening electrons and the nucleus.

If an electron is at a great distance from the nucleus and its path is beyond the orbits of the inner shell or shells, the effective charge of the nucleus is $(Z - N)e$, where Z is the atomic number, N is the number of



Fig. 3-8 A three-electron atom with the third electron occupying a non-penetrating orbit.



Fig. 3-9 A three-electron atom with the third electron occupying a penetrating orbit.

electrons in the screening shell, and e is the charge of the electron. This being true, we can modify Eq. (2·13), which denotes the total energy of the electron in the hydrogen atom, to fit the energy requirements of an electron of the foregoing description. The equation then becomes

$$E^n = - \frac{2\pi^2(Z - N)^2 e^4 m}{n^2 h^2}$$

If it is assumed that the third electron in the lithium atom follows a path outside both the nucleus and the orbits of the two first-quantum electrons, the effective charge of the nucleus may be postulated as consisting of the nucleus proper plus the two inner electrons. Considered from this structural viewpoint, the outer electron moves about a nucleus which has a single positive charge and which is equivalent to that of the hydrogen nucleus. A diagrammatic representation of such a non-penetrating orbit is given in Fig. 3.8.

Should the third electron in the lithium atom follow a path which penetrates the orbits of the two first-quantum electrons, the effective charge of the nucleus will no longer be $+1$. As the electron penetrates the orbitals of the inner electrons, the latter's screening effect is decreased and the attractive force of the nucleus becomes greater than $+1$. On the other hand, the effective charge of the nucleus will never be $+3$, which is the actual value of the nuclear charge of the lithium atom, because the outer electron will move part of the time outside the orbits of the two inner electrons. The greater the amount of penetration, the stronger is the attractive force exerted by the nucleus; consequently the

greater will be the ionization potential. The effective nuclear charge will be a value less than +3 but greater than +1. A schematic representation of a penetrating orbit is given in Fig. 3.9.

3.20 Electronegativity. The attraction of a neutral atom in a stable molecule for electrons is a property that Pauling designates as *electronegativity*. We shall have occasion to discuss this property in more detail in Sec. 4.17, but for the present it will suffice to consider it in the light of a periodic property. From heats of formation of the most common elements in their compounds Pauling has set up an arbitrary electronegativity scale (Table 3.17) for the atoms of the elements. This scale varies from 0.7 for cesium to 4.0 for fluorine. From the relative positions of the

TABLE 3.17 ELECTRONEGATIVITIES OF THE ELEMENTS

Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.3	Sn 1.7	Sb 1.8	Te 2.1	I 2.5
Cs 0.7	Ba 0.9					

elements on this scale a prediction can be made as to the ease with which the atoms of the elements lose their valence electrons. Electronegativity is a property of the elements which is a periodic function of their atomic numbers. Table 3.17 is an arrangement of some of the common elements in the order in which they fall in the Mendeleev periodic classification and includes Pauling's values for the electronegativities of these particular elements. It can be seen that the periodicity of electronegativity follows the pattern of most of the other periodic properties. Upon progressing from left to right along any row of these elements (Table 3.17) the magnitude of the electronegativity increases, whereas, in passing from the top downward in any group, there is a progressive decrease in the values for electronegativity.

3.21 Other Chemical Properties. As we have said before, there are two structural properties, the size of atoms (or ions) and the ease of removal of electrons, which largely determine the chemical properties of the elements. The periodic nature of these fundamental properties has been described in detail in the preceding sections. However, we shall

attempt to summarize some of the more important relationships indicated by the periodic table in connection with chemical properties.

First of all, as we progress across the periodic table from left to right, we find that the metallic character of the elements in any period decreases, whereas the nonmetallic properties increase. Thus, as the radii of the atoms of the elements decrease, in passing along a given period, they tend to hold their outer electrons more tightly. As a general rule, large atoms are found in elements that are metals, and small atoms are found in elements that are nonmetals. Consequently the best reducing elements are the metals which lose electrons easily to form positive ions, and the latter form basic hydroxides because of their relatively small attraction for electrons. In general the electronegative character of the elements increases along any series. Hence the metals on the left of the periodic table form basic oxides, and conversely the nonmetals, on the right, form acidic oxides. This accounts for the fact that the positive ions may exist in water solution with hydroxide ions and the negative ions may be found in water solution with a high concentration of hydronium ions. A less accurate description would classify the metals as base-forming elements and the nonmetals as acid-forming elements. It is also true that, when an element exhibits two or more valences, the ion of the element in its lowest valence is less electronegative than in a higher valence. For example, the stannous ion is more basic in its properties than the stannic ion, as indicated by the fact that stannic sulfide will dissolve in potassium hydroxide solution, whereas stannous sulfide will not.

The metallic character of the elements increases in passing from the top to the bottom of the periodic table. Probably the best illustration of this tendency is found in Group V, in which nitrogen, a nonmetallic element, occurs at the top and bismuth, a metal, is found at the bottom. In other words, the more acid-forming elements are found at the top of the table, and the stronger base-forming elements occur at the bottom of the table. Again in Group V, the hydroxide of phosphorus is definitely an acid, whereas the hydroxide of bismuth must be classified as a base.

The size of an atom and the ease with which it loses electrons may also determine the type of bond that is formed when the element enters into chemical reaction. These relations are discussed in Chap. 4.

EXERCISES

1. From a periodic table select as many sets of triads as possible which are similar to those of Döbereiner.

2) Upon what basis did Newland propose the law of octaves? Why could this law not be applied for producing a satisfactory classification of the elements as we now know them?

158 Fundamental Concepts of Inorganic Chemistry

3. Suggest Mendeleev's reasons for reversing the order of atomic weights in placing tellurium and iodine in the periodic table.

4. Upon what basis did Mendeleev arrange the elements in his periodic table? How does this basis differ from the one used in more recent tables?

5. Enumerate some of the obvious weaknesses of the Mendeleev classification of the elements.

6. State the periodic law as formulated by Mendeleev. Why is this statement somewhat invalid in view of present scientific knowledge?

7. What was Moseley's contribution to the construction of an accurate periodic table?

8. What is the relationship, if any, between atomic weights and atomic numbers?

9. Recalling the discussion concerning isotopic mixtures of atoms among the various elements, as given in Chap. 1, account for the fact that the atomic weights of tellurium and iodine are not in the same order as their atomic numbers.

10. What valences are said to be characteristic of each group of elements in the periodic table?

11. What is a group? How do the properties of the elements vary within a group?

12. What is a period? How do the properties of the elements vary as the atomic weight increases?

13. How does it happen that periodic tables are divided into short periods and long periods?

14. Explain the present-day usefulness of periodic tables. How have such tables been of even greater service in the past?

15. To what extent, if any, is the extended form of the periodic table an improvement over the Mendeleev type?

16. Distinguish between the four general types of elements, and explain how their chemical properties differ.

17. Distinguish between the transition elements and the rare earth elements.

18. What is meant by the term lanthanide contraction?

19. List several properties of the elements, physical and chemical, which are periodic functions of atomic numbers.

20. Indicate the changes in chemical properties which accompany increase in atomic number of the elements within one of the short periods.

21. In which columns of the periodic table are maximum melting points among the elements encountered?

22. In terms of atomic size and electronic structure indicate the change from metallic to nonmetallic properties which may be observed in some periodic groups.

23. How does the electron structure of atoms of metals differ from that of atoms of nonmetals?

24. Explain the location of the light metals, the heavy metals, and the nonmetals in the extended form of the periodic table.

25. In what region of the extended periodic table would you expect to find metals with the greatest tensile strength?

26. How does the electrical resistance among the elements of a given row in the extended form of the periodic table vary in passing from left to right?

27. From their positions in the periodic table predict the chemical properties of astatine and francium.

28. Upon the basis of the pattern of change within a group of the periodic table explain how cesium should differ from sodium.

29. From the relative position of radium in the periodic table predict the solubilities of its hydroxide and sulfate.

30. In what region of the periodic table are located those elements which have a tendency to form strong oxygen acids?

31. How do the ionization potentials of the elements vary in the periodic table? Where are the elements with the greatest electron affinity found? Where are those with the least electron affinity located?

32. How does the property that Pauling defines as electronegativity vary within the periodic table?

33. Explain the small differences in the sizes of the atoms of Cu, Ag, and Au and their ions as compared with the large differences in the sizes of the alkali metal atoms and their ions. These differences are forcibly exhibited in the Campbell periodic table.

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CHAPTER 4

Forces between Atoms

Chemistry is concerned with the structure, properties, and reactions of substances. The building blocks which make up substances are the atoms of the several elements. These building blocks—atoms—may be assembled and held together in a variety of ways, resulting in the formation of hundreds of thousands of different compounds. However, amid this multitude of compounds, definite types may be distinguished, and the basis for such distinction is dependent upon the various forces which hold the components of compounds together.

THE ORIGIN OF THE CHEMICAL BOND

Many factors influence the manner in which two atoms unite and the type of bond that is formed. Among these are the nuclear charges, the distribution of electrons in the various shells, and the radii of the combining atoms. Such factors differ for atoms of different elements; therefore these variables multiplied by the number of chemically active elements indicate the different types of chemical bonds that are possible. In other words, the atoms of each element differ from the atoms of all other elements, to some extent, in the fashion in which they combine with other atoms. The complexity arising from so many bonding possibilities results in the discouraging fact that there is no simple, collective way of describing the manner in which atoms unite.

Pauling¹ divides chemical bonds roughly into three extreme types: electrostatic bonds, covalent bonds, and metallic bonds. This division is based largely upon the mechanism of formation and the properties of each type of bond. It is a loose classification since there are so many intermediate types which represent a transition between the extremes. Despite the oversimplification implied in this classification it is quite useful for an elementary approach to the problem of chemical binding.

4-1 Introduction. The formation of a bond between two atoms is due to some redistribution, regrouping, or orientation of their electrons to

¹ Linus Pauling, "The Nature of the Chemical Bond," p. 3, Cornell University Press, Ithaca, N.Y., 1940.

form a more stable arrangement. The bonding abilities of the atoms of the various elements depend largely upon the extent to which their electron shells are completed. By the "completion" of a shell we mean agreement between the number of electrons it contains and the number in the corresponding shell of the noble gas of next higher or lower atomic number. Atoms of these elements (Table 2-3) contain a total of 2, 10, 18, 36, 54, and 86 extranuclear electrons. Apparently electron totals of these magic numbers impart a greater electronic stability than may be achieved by any intermediate numbers, inasmuch as the noble gases are so inert that they form no chemical combinations.

Upon the basis of complete and incomplete electron shells four types of atoms may be recognized. A description of these types is given in Sec. 3-7, but some recapitulation of this classification seems necessary to introduce a discussion of the present concepts of chemical binding. Type I elements are the inert gases with stable electronic configurations whose atoms are attracted by feeble electrostatic forces, usually designated as van der Waals forces (Sec. 4-26), but which do not enter into chemical combinations. Type II elements are composed of atoms whose outermost shells contain fewer than eight electrons and are therefore incomplete in comparison with the outermost shells of the noble gases. Forces operating between these atoms will be discussed more completely within this chapter. Type III elements contain atoms with two incomplete outermost shells; because of this structure, such elements may enter into chemical combinations in a variety of ways. Mention of these elements is made in Sec. 4-3, and an extended discussion of the compounds they may form is given in Chap. 5. Type IV elements are those of the lanthanide and actinide series, the atoms of which have three outermost shells that are incomplete. The differentiating electrons of the atoms of these elements are in the third from the outermost shell, and the expansion of a shell so deeply seated within these atoms produces very little variation in their chemical properties. On the other hand, the expansion of the innermost, incomplete shell gives rise to a contraction in the atomic volumes of the atoms (Sec. 3-13). We shall not have occasion to mention these elements again in connection with binding forces.

4-2 The Rule of Eight. In his periodic table of 1871 (Sec. 3-5) Mendeleev implied the existence of a relationship between the positions of the elements within the table and their valencies. This idea was expanded by Abegg in 1904 (Sec. 3-16) in producing his rule of eight. Abegg ascribed to every element certain positive and negative valencies, which he also designated as normal valencies and contravalencies. In his own words¹ he concludes: "Every element has both a positive and a negative maximum valency, the sum of which is always 8, and the former

¹ R. Abegg, *Z. anorg. Chem.*, **39**: 330 (1904).

corresponds to the group-number." Since 8 seemed to be the maximum valence of an element, Abegg considered this to be the total number of electrons that an atom could accommodate. Furthermore he conceived the atom as having a structure which permitted the attachment of no more than this number of other atoms.

In 1916 W. Kossel and G. N. Lewis independently advanced the first definite hypotheses concerning the mechanism of atomic binding. Although both hypotheses employed the idea that atoms acquire positive valence by losing electrons and negative valence by gaining them, the former dealt largely with polar linkages, whereas the latter was more concerned with nonpolar bonding. Moreover Kossel used the dynamic model of the atom, as proposed by Bohr, in explaining forces between atoms, while Lewis resorted to a static model, of cubic structure, with eight points of attachment for other atoms.

Kossel pointed out the facts that an element preceding an inert gas, in the periodic classification, is always strongly electronegative and the element immediately following is electropositive, both elements being univalent. Furthermore the two elements preceding and following the foregoing univalent elements were divalent and possessed of polar characteristics similar to their immediate neighbors. For example, potassium and calcium are univalent and divalent, respectively, and electropositive in nature, whereas chlorine and sulfur possess equivalent valencies to the preceding elements but are electronegative in character. To explain these facts, Kossel postulated that the structure of an inert gas represented a stable arrangement of electrons which other elements sought to attain by gaining or losing the necessary number of electrons. According to his theory the valency of an electronegative atom is the number of electrons it must gain or, if electropositive, the number it must lose to attain the electronic structure of the nearest inert gas. The essential feature of Kossel's explanation was based upon the tendency of two atoms, dissimilar in their polar characteristics, to combine in a process by which one tended to lose and the other to gain electrons. Support to this theory has since been given by experimental results obtained through various methods of instrumental analyses, particularly the X-ray examination of crystals. The bonds in crystals of KCl and CaS can be explained as arising from the electrostatic attraction between the constituent ions. Accordingly Kossel's theory is quite satisfactory for the electrovalent bond which may exist between the lighter elements that are not far removed from the inert gases in their atomic numbering.

The Kossel theory of electronic transference between dissimilar atoms to form ionic linkages was incapable of explaining the nonionic bonding which may exist between either similar or dissimilar atoms. For example, the binding in NaCl can be explained as arising from the loss of one elec-

tron by the sodium atom and the gain of one electron by the chlorine atom. In this transfer sodium, as an ion, has attained the electronic structure of neon and chlorine the structure of argon. The bond is one of electrostatic attraction between the oppositely charged ions. On the other hand the chlorine atom may combine with another chlorine atom to form the chlorine molecule, and the linkage is clearly a nonionic bond which does not involve a transfer of electrons. In like manner four chlorine atoms may combine with one carbon atom to form the nonionic molecule, carbon tetrachloride. To G. N. Lewis goes the credit for the first explanation of nonionic binding.

In his theory Lewis utilized the same concept as the one advanced by Kossel in explaining the loss and gain of electrons in the formation of ionized compounds. For nonionized compounds Lewis suggested that atoms of two elements may share electrons in striving to attain the inert gas structure. To distinguish the two different types of binding, Langmuir at a later date proposed the terms *covalency* to designate the process of sharing electrons and *electrovalency* to indicate the bond produced by electron transfer. According to the Lewis theory an atom in forming a covalent bond must share not only an electron belonging to another atom but also one of its own electrons with the other atom. Thus the covalent bond is one produced by the sharing of two electrons by two atoms. For instance, the chlorine molecule is composed of two atoms of chlorine held together by a bond composed of two shared electrons. Each chlorine atom originally had seven electrons in its outermost shell, but by the mutual sharing of two electrons both atoms have attained the electronic structure of the inert gas argon. Furthermore the maximum number of covalent bonds which an atom can form is limited by the number of electrons available, or needed, in its outermost shell; therefore covalency and electrovalency are numerically equal. For example, the carbon atom has four electrons in its valence shell and consequently may form a maximum of four covalent bonds with four atoms such as chlorine. In the carbon tetrachloride molecule so produced the carbon atom by sharing four electron pairs has acquired the electronic structure of neon, while each of the chlorine atoms has attained the argon configuration.

4.3 The Pairing of Electron Spins. The rule of eight, as interpreted by Kossel and Lewis, has had a profound influence upon the development of theories for atomic structure and upon explanations for chemical reactions. However, the octet rule is by no means universal. It applies only to the Type II elements (Sec. 3-7), and, even among these, there are well-known exceptions. For example, the compounds BeCl_2 and BCl_3 have properties characteristic of covalent compounds; yet neither the beryllium nor the boron atom has attained eight electrons in the valence shell by forming these compounds. Other exceptions include PCl_5 and

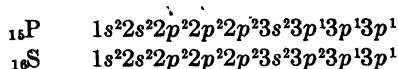
SF₆. In short the octet rule—which has its uses in an elementary discussion of valency—oversimplifies the factors involved in the formation of many chemical bonds. A better basis for predictions in regard to bond formation is one that utilizes the concept of uncompleted orbitals in one atom which may be filled by electrons from another atom.

It will be recalled from Sec. 2-24 that the term *orbital* is used to designate the orbits for paired electrons of opposite spins, the two electrons being identical in terms of their other quantum numbers. Furthermore electrons so described are also virtually identical in terms of their kinetic and potential energies. In the explanation of electron distributions (Sec. 2-25) it was assumed that during the process of atom building one electron goes into each possible orbital of a given sublevel until each of the orbitals in that sublevel contains one electron, all single electrons being of parallel spins (spins in the same direction); then another electron is added to each orbital to form paired electrons, until each orbital contains two electrons. The opposed spins of the coupled electrons result in an electromagnetic attraction which is more than sufficient to overcome the electrostatic repulsion of the two negative charges of the same two electrons. The general idea of atomic synthesis can be utilized to explain chemical binding between atoms.

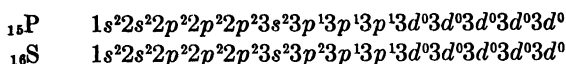
Table 2-2 shows the distribution of electrons among the various possible quantum levels of an atom, and Table 2-3 shows the actual distribution of electrons in the atoms of the various elements. From these tables it may be concluded that all atoms, except those of the inert gases, contain uncomplete orbitals. The term *uncomplete* is used to describe orbitals which are either unoccupied or incomplete. An unoccupied orbital contains no electrons, whereas an incomplete orbital possesses one electron. Moreover an uncomplete orbital may be either stable or unstable depending upon the total electronic distribution of the particular atom. One theory of chemical binding postulates that uncompleted orbitals in one atom may be filled by electrons from another atom.

The pairing of electron spins by two electrons to produce a bond between two atoms is frequently referred to as the *rule of two*, inasmuch as the completed orbital contains two electrons. Accordingly an atom with an incomplete stable orbital, containing one electron, tends to acquire an electron of opposite spin from another atom to complete the orbital. If the acquired electron is completely removed from its parent atom, the bond becomes an electrovalent bond. On the other hand, if the electron pair produces completed orbitals in two atoms, the coupled electrons will be shared mutually and the bond is a covalent one. Furthermore a stable unoccupied orbital may be filled by an electron pair from another atom to produce another form of electron sharing. This latter linkage is usually described as a *coordinate* bond (Sec. 5-5).

For specific illustrations of the pairing of electron spins by electrons from two different atoms, let us consider some of the chemical combinations of the elements phosphorus and sulfur. The atoms of these two elements may be indicated symbolically as



In this representation the numbers designate the principal shells, the letters indicate the subshells, and the superscript numbers give the number of electrons in each orbital. The repetition of numbers and letters designates the number of orbitals in each subshell. Hence it can be seen that the phosphorus atom contains four orbitals in its valence shell, the s orbital of this shell contains a pair of electrons, and the other three orbitals contain single electrons. In the case of sulfur there are four orbitals in the valence shell, two of which contain electron pairs and the other two, single electrons. From Table 2-3, which shows the distribution of electrons in quantum groups, and from Fig. 2-20, which indicates the approximate stability sequence for atomic orbitals, we may predict that both the phosphorus and the sulfur atoms have five unoccupied orbitals in the d subshell. If these unoccupied orbitals are designated as d^0 each, then the symbolic representations of these atoms are



Considering the outermost shells of the phosphorus and sulfur atoms, the foregoing representations indicate that phosphorus has a complete orbital in the $3s$ subshell, three incomplete orbitals in the $3p$ subshell, and five unoccupied orbitals in the $3d$ subshell; sulfur has a complete orbital in the $3s$ subshell, one complete and two incomplete orbitals in the $3p$ subshell, and five unoccupied in the $3d$ subshell. Theoretically a maximum of nine covalent bonds should be formed by the nine possible orbitals of the $n = 3$ energy level (M shell), but spatial limitations due to the volumes of the atoms concerned limit the number of atoms which can be bonded to the central atom.

Phosphorus and sulfur enter into chemical combinations to fill either the incomplete or the incomplete and some of the unoccupied orbitals. The filling of only the incomplete orbitals accounts for compounds such as H_2S and PH_3 . The filling of incomplete and some unoccupied orbitals produces the bonding found in PCl_5 and SF_6 . In phosphorus pentachloride the phosphorus atom has formed five covalent bonds. In forming these bonds the three incomplete $3p$ orbitals are completed, and the electron pair of the $3s$ orbital is uncoupled to form two additional bonds with the chlorine atoms. The uncoupling of the $3s$ electron pair to pro-

duce additional bonds causes an expansion of the atom to utilize one of the $3d$ orbitals. The process of uncoupling an electron pair requires considerable energy, but the stability of PCl_5 indicates that the reaction produces more than sufficient energy for this purpose. In sulfur hexafluoride the paired electrons in the $3s$ and $3p$ orbitals are uncoupled, in addition to the two $3p$ electrons, to make six electrons available for bond formation. Therefore two of the $3d$ orbitals are utilized in forming the six covalent bonds formed by sulfur in this compound.

A more detailed discussion of the various theories which have been advanced to explain the electron distribution in covalent bonding is given in Sec. 4-11.

✧ THE IONIC BOND

The ionic, or electrovalent, bond is produced when one or more electrons has been transferred from one atom to complete the orbitals of another atom. According to the older octet theory the formation of electrovalency arises from the loss or gain of atoms in attaining the closed electronic shells, which are characteristic of the inert gas atoms. However, as has been explained before, the octet idea can be applied only to the Type II elements (Sec. 3-7). Furthermore ionic linkages are largely confined to chemical reactions between elements with comparatively low ionization potentials and elements with comparatively high electron affinities. Elements so described are those which immediately precede and those which closely follow the noble gas elements in the periodic classifications. In other words, an atom with a nearly filled outer shell tends to accept electrons, whereas an atom with only one or two electrons in its outermost shell tends to give them up. On the other hand, elements with atomic shells which are about one-half filled achieve closed shells by sharing electrons when they combine with other elements. For example, bonds formed between elements such as F and Cs are essentially ionic, while those formed by elements like carbon are largely covalent. Pure bond types, ionic or covalent, as described may never exist, but the use of these terms is convenient for discussion. Usually bonds are intermediate in type and possess characteristics which are in between the two extremes.

✧ **4-4 General Characteristics of the Ionic Bond.** For the Type II elements the electrovalent bond arises from the particular properties of completed s and p sublevels. Ions produced from these elements have attained the electronic configuration of the inert gases. Thus the formation of a sodium ion from a neutral sodium atom results in an inert gas structure of $1s^2 2s^2 2p^6$. Inasmuch as the orbits of the second quantum level (second shell) are completed, the resultant orbital angular momen-

tum (motion about the nucleus) and the resultant electronic-spin angular momentum (the spin of the electron about its own axis) are equal to zero.] Therefore the attraction, or interaction of any kind, toward the electrons of other atoms is at a minimum. In this connection it may be stated that two oppositely charged ions in close proximity to each other will exert a mutual electromagnetic effect on the two respective electronic systems, in such a manner that they may be deformed or distorted to a degree depending upon the charges and volumes of the ions concerned. Ions with large charges produce great distortion, and the electrovalent link may be converted into a covalent link.

The electrovalent bond results from a coulombic attraction between the excess charges on the oppositely charged ions. The strength of the bond is roughly proportional to the product of the charges on the ions and inversely proportional to the square of the distance between the effective centers of the ions. This is not a true bond in a strict interpretation of the word, in that it is neither rigid (in the sense of nonelastic) nor directed. The electrostatic fields of the ions extend in all directions; consequently a crystal of an ionic compound such as sodium chloride, which has a cubic lattice, is composed of a cluster of ions in which there is an arrangement of six chloride ions grouped spatially about each sodium ion and six sodium ions grouped around each chloride ion. The number of ions which may be grouped around a central ion is determined by the radii of the respective ions involved.

Ions carrying high charges are rare because of the extremely large amounts of energy involved in transferring electrons from one atom to another. Moreover a positive ion of high charge and small volume will exert a great distorting effect on a negative ion, with a resulting possibility of a covalent bond formation. In fact a high charge can be maintained only where the ionic volume is high, since with low ionic volume the tendency to recapture electrons to produce covalent links is to be expected.

The conditions predicting the kind of valency, ionic or covalent, which may arise, are summed up in *Fajans' rules*. These rules are indicated in tabular form as:

<i>Electrovalency</i>	<i>Covalency</i>
Low positive charge	High positive charge
Large cation	Small cation
Small anion	Large anion

According to Fajans' rules electrovalency appears only in elements which have lost few electrons; however, this is again dependent upon the volume of the anions. Thus the compound SnF_4 is undoubtedly ionic in nature, whereas the compound SnCl_4 is probably covalent.

4.5 Ionization Energy and Electron Affinity. Whether or not an atom will enter into chemical combination depends upon the amount of energy necessary to establish a bond between this atom and another atom. Likewise, the type of bond which may be formed is dependent upon the amount of energy necessary to remove an electron completely from the atom and the amount of energy that is available when this electron is added to an orbital of another atom. The preference of elements for the formation of electrovalent or covalent bonds can be predicted in a general fashion from the electronic structure of the atoms concerned.

The highly stable helium atom contains two electrons which are paired (of opposed spins, which produce an electromagnetic coupling) in the $1s$ orbital. The removal of an electron from the helium atom involves uncoupling the electron pair and lifting the electron against the attractive force of the nucleus. The total energy for the process of removing one of the electrons from the helium atom is 570 kcal/gram atom. This may be compared with the values of 312 kcal/gram atom to remove an electron from the hydrogen atom and 117.9 kcal/gram atom to remove an electron from the sodium atom. Table 4-1 gives energy values for the removal of an electron from other atoms. Ordinary chemical reactions do not involve sufficient energy changes to remove electrons from helium atoms either completely or incompletely. Nor can the electron be removed from the hydrogen atom, by chemical action, to form an electrovalent bond between a positively charged hydrogen ion and another ion which is negatively charged, because of the large amount of energy necessary for this process. However, the electron is incompletely removed from the hydrogen atom to form a covalent bond between the hydrogen atom and another atom; for example, $H:Cl$ is a covalent compound produced by such a bonding. The amount of energy necessary to remove the unpaired electron from the sodium atom is available in many chemical reactions; consequently sodium atoms react readily with many atoms and molecules to produce sodium ions.

Covalent bonds may be formed by atoms when less energy is available than is necessary to remove an electron completely from the valence shell. This statement does not imply that the bond energy is less for the covalent bond than for the electrovalent bond. It simply prophesies that, when the available energy is not sufficient for the formation of an electrovalent bond, a covalent bond may be formed. Actually the energies of the covalent and ionic bonds are difficult to compare because the factors involved in them are different. But the heat of dissociation of a covalent compound and the energy of formation of ionic crystals from gaseous atoms are comparable. The heat of dissociation of hydrogen molecules into atoms is 103 kcal/mole, and the energy of formation for

solid sodium chloride from its gaseous atoms is 98.2 kcal/mole. Such values indicate that the bond energies of covalent and electrovalent compounds are of the same general magnitude.

The formation of a positive ion by the removal of one or more electrons from a neutral atom involves the expenditure of a considerable amount of energy, since the electron or electrons must be removed against the electrostatic attraction of the resulting positive ion. The energies of ionization in kilocalories per gram atom per electron (the amount of energy necessary to remove one electron per atom for a gram-atomic weight) for some of the univalent elements are given in Table 4-1.

TABLE 4-1 MEAN IONIZATION ENERGIES AND ELECTRON AFFINITIES

Element	Ionization energy, kcal/gram atom	Electron affinity, kcal/gram atom
F	429 0	98 5
Cl	298 9	86 5
Br	272 1	81 5
I	240 8	74 2
H	312 0	16 5
Li	123 8	Assumed zero
Na	117 9	Assumed zero
K	99 7	Assumed zero
Rb	95 9	Assumed zero
Cs	89 4	Assumed zero

Neutral atoms, which tend to acquire electrons to fill incomplete orbitals, release energy in exhibiting the property of *electron affinity*. For example, the chlorine atom readily acquires one electron with the release of 86.5 kcal/gram atom. The electron affinities of some other atoms which tend to form univalent negative ions are given in Table 4-1.

In the chemical union of two atoms the values for the ionization energy and electron affinity of the reacting elements are rarely equal or even approximately the same. As a general rule the ionization energy is much greater than the electron affinity. However, the comparative values for the energies involved in these two processes suggest a possible prediction as to whether the resulting compound will be electrovalent or covalent. If the difference in energy is small, as in the formation of sodium chloride from neutral atoms of sodium and chlorine,

$$117.9 - 86.5 = 31.4 \text{ kcal}$$

the deficiency of energy necessary to transfer the electron is supplied by a release of energy in the process of setting up the electrostatic bond between the two ions as they are brought together. When the difference

is great—so great that the difference cannot be supplied by energy released in the building up of the crystal lattice or in the process of solvation—the compound produced will be either partly or almost completely covalent. Examples of such compounds are beryllium chloride, BeCl_2 , and boron trichloride, BCl_3 . The ionization energy necessary for the removal of two electrons from 1 gram atom of beryllium is 636 kcal. The energy supplied from 2 gram atoms of chlorine is 173 kcal. Subtracting 173 from 636 kcal leaves a difference of 463 kcal. This difference may be, in part, supplied by the lattice-building energy released or by the solvation energy produced by solution (the solvation energy of the beryllium ion is quite high), but beryllium chloride is partly covalent, as is indicated by its solubility in benzene and the low conductivity of the molten compound. The compound boron trichloride is almost completely covalent. The ionization energy necessary to remove three electrons from a gram atom of boron is 1620 kcal. The addition of 3 gram atoms of chlorine supplies 259.5 kcal of energy. The difference between the two values is 1360.5 kcal, which is a value too large to be supplied by any other process in connection with the reaction. Therefore, the atomic binding between the boron atom and the chlorine atoms is one in which the electrons are shared and not exchanged.

4.6 Lattice Energy. The crystal, or lattice, energy of an ionic compound may be defined as the energy required to separate a formula weight of its ions by infinite distances. Conversely, it is also the energy released when a formula weight of a substance is produced by bringing together from infinite distances the necessary number of positive and negative gaseous ions.

Whether an ionic or a covalent compound is formed in the chemical union of atoms is dependent, not only upon the difference between the amount of energy released due to electron affinity and the amount of energy required for ionization, but also upon the lattice energy of the salt produced. The setting up of electrostatic forces between ions in a crystal is an exothermic process, as evidenced by the energy necessary to convert a crystal to a molten condition by heat. The lattice energy is available to supply the difference between ionization energy and electron affinity, as explained in the preceding section.

Solid ionic compounds are not made up of individual molecules. Instead the crystal lattice is built up by the deposition of a regular array of ions in which each ion is surrounded by a definite number of ions of opposite charge. For example, a crystal of sodium chloride may be regarded as a huge cluster of ions in which six chloride ions are grouped spatially around each sodium ion and six sodium ions are grouped around each chloride ion. The number of ions which may be grouped around a central ion is determined by the radii of the respective ions involved. In

the vapor state, however, ionic compounds are essentially molecular in composition. Such molecules, as, for example, NaCl, are polar (Sec. 4.16) in their structure and can be considered as ion pairs, in which the portion of a molecule occupied by the sodium atom is positively charged and that part containing the chlorine atom is negatively charged. The pair of ions in a gaseous molecule of an ionic compound are probably held together at an equilibrium distance from each other as a result of a balance between the forces of attraction (between the two oppositely charged ions) and the forces of repulsion which come into play at short distances.

According to Coulomb's law of electrostatic attraction the force operating between two charged bodies m_1 and m_2 is $-m_1m_2/r^2$. Upon integrating this equation between the limits of r and infinity the expression becomes m_1m_2/r . The latter equation expresses the *potential energy* of a system containing the same two charges and represents the energy needed to move one charged body from an infinite distance to a distance r from the second body. Consequently the electrostatic potential energy of two oppositely charged ions may be expressed as

$$PE_{\text{electrostatic}} = \frac{z_1 z_2 e^2}{r} \quad (4.1)$$

where the z values represent the integral charges on the two ions, e is the charge on the electron, and r is the distance between the centers of the two ions. However, Eq. (4.1) represents only the electrostatic energy between two ions, whereas, within a crystal, the same two ions are subjected to additional coulombic forces from other ions. Furthermore ionic crystals are not composed of simple ion pairs, but of ionic clusters in which each cation is surrounded by a definite number of anions, and each anion is likewise encompassed by a fixed number of cations. Therefore, in order to calculate the coulombic energy of any single ion, allowance must be made for the number and arrangement of neighboring ions of both signs. Because of electrostatic interactions with surrounding ions the coulomb energy of a single ion is greater than indicated in Eq. (4.1) by a factor typical of each kind of crystal structure. This factor, known as the *Madelung constant* and designated as A , is the summation of the electrostatic contributions of neighboring ions and depends on the type of lattice in which the ion occurs. It is beyond the scope of this discussion to include the mathematical derivation for these contributions, but as a result of this summation the coulombic energy of a single ion may be indicated as $-A \cdot e/r$. The electrostatic potential energy per ion pair is

$$PE_{\text{electrostatic}} = -\frac{Az^2e^2}{r} \quad (4.2)$$

where A is the Madelung constant and the negative sign indicates that energy is released when the two ions station themselves within the crystal.

The Madelung constant is a correction factor to take care of additional electrostatic forces exerted by neighboring ions upon an ion pair and is entirely dependent upon the geometry of the crystal. The Madelung constants for a few simple crystal lattices are given in Table 4-2. The

TABLE 4-2 VALUES OF MADELUNG CONSTANTS
Crystal structure Madelung constant

Sodium chloride	1 747558
Cesium chloride	1 762670
Sphalerite, ZnS	1 63806
Wurtzite, ZnS	1 641
Calcium fluoride (fluorite)	5 03878
Rutile, TiO ₂	4 816
Cadmium iodide	4.71

Madelung constants for structures containing divalent ions, such as calcium fluoride and cadmium iodide, are much greater than those for structures containing monovalent ions, as sodium chloride and cesium chloride, or those for structures in which the bonding is partly covalent, as in zinc sulfide.

In addition to the coulombic forces which operate between ions there are repulsive forces which arise to prevent ions from approaching each other too closely. These forces originate as a result of a general mutual repulsion of the electron clouds of atoms and ions whenever these clouds penetrate each other and the electrons do not form a bond with a common electron pair. As a result of the repulsive forces opposing those of coulombic attraction, oppositely charged ions come to equilibria at definite distances from each other. The forces of repulsion become strong when the electron shells of two ions are in close contact but decrease rapidly with distance. The factor of repulsion is difficult to calculate and is usually represented as B/r^n , where B is a constant and n is the power of the distance to which r (the distance between ions) must be raised to give the correct repulsive force.

The total lattice energy per "ion pair" within a crystal of the MX type may be indicated as

$$U_{MX} = - \frac{Az^2e^2}{r} + \frac{Be^2}{r^n} \quad (4.3)$$

and the total lattice energy per formula weight of MX is

$$U_0 = - N \frac{Az^2e^2}{r} + N \frac{Be^2}{r^n} \quad (4.4)$$

where U_0 is the lattice energy and N is Avogadro's number. Actually in a

formula weight of an ionic compound composed of two oppositely charged ions, such as sodium chloride, there are $2N$ ions, but the use of N is justified inasmuch as the interionic attraction occurs between pairs of ions and necessitates the division of $2N$ by 2.

In those crystal types where r and n can be determined experimentally it is possible to calculate the repulsive coefficient B , and if we omit some of the mathematical steps involved, a more general equation for lattice energy may be stated as

$$U_0 = \frac{NAe^2z^2}{r} \left(1 - \frac{1}{n}\right) \quad (4.5)$$

The lattice energies of the alkali halides have been calculated with the aid of formulas of this type and have been found to be in close agreement with those values which have been determined experimentally. These calculated values are included in Table 4-3 and serve to indicate the magnitude of the lattice energy.

TABLE 4-3 LATTICE ENERGIES KILOCALORIES PER FORMULA WEIGHT, OF THE ALKALI HALIDES

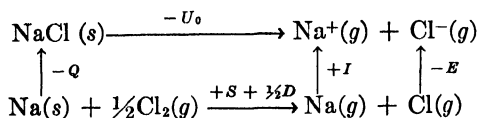
Elements	Fluoride	Chloride	Bromide	Iodide
Lithium	240 1	199 2	188.5	174 1
Sodium	213 4	183 1	174.5	163.9
Potassium	189 7	165.4	159.3	150.8
Rubidium	181 6	160 7	153 5	145.3
Cesium	173.7	152 2	146 3	139 1

4.7 The Born-Haber Cycle. The lattice energy of an ionic compound is the energy set free when the crystal lattice is formed from free gaseous positive and negative ions. The process of gaseous ions condensing to form ionic crystals is of rare occurrence and is therefore largely of theoretical interest only. It will be recalled from Sec. 4-5 that the difference between the ionization energy and the electron affinity of two reacting elements may be supplied by the lattice energy released in producing the ionic crystal. In other words, the lattice energy is one of the energy factors entering into the stabilization of an ionic bond.

The direct determination of the lattice energy of an ionic crystal has been carried out for only a few compounds. In the majority of cases it is not possible to measure this energy directly; however, a cyclic process has been devised by Born and Haber which relates the crystal energy to other thermochemical quantities. Where the energy of formation of a crystal from its component elements is known, it is possible to dissect this value into the energies of a number of processes, which may be postulated as constituting the intermediate steps in the formation of the crystal. By

174 Fundamental Concepts of Inorganic Chemistry

means of this circuitous procedure it is possible to calculate algebraically the theoretical lattice energy of a crystal. For example, consider the formation of sodium chloride from elementary solid sodium and elementary gaseous chlorine. It may be assumed that the sodium metal is evaporated and the diatomic chlorine is dissociated; then the alkali atoms are ionized, and the electrons so obtained are transferred to the halogen atoms so that positive sodium ions and negative chloride ions are left in the gaseous phase. As indicated diagrammatically, the energy of sublimation of metallic sodium is S , the ionization energy of gaseous sodium is I , the energy of dissociation of Cl_2 is D , the electron affinity of the chlorine atom is E , and the lattice energy of solid NaCl is U_0 . The heat of formation of the crystals from its elementary elements is designated as Q .



The total energy of formation of the crystal from its elementary components is given by the equation

$$-Q = S + \frac{1}{2}D + I - E - U_0$$

The value of Q is accurately known experimentally for many substances, and where the other thermochemical values are available, it is possible to solve for the lattice energy by rearranging the foregoing equation as follows:

$$U_0 = Q + S + \frac{1}{2}D + I - E$$

The calculation of the lattice energy of sodium chloride may be completed by substituting experimental data as follows:

$\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s), Q$	98.2 kcal/gfw
Sublimation energy of sodium metal, S	26.0 kcal/gfw
Dissociation energy of molecular chlorine ($D = 57.2$ kcal/gfw), $\frac{1}{2}D$	28.6 kcal/gfw
Ionization energy of sodium atom, I	117.9 kcal/gfw
Electron affinity of chlorine atom, $-E$	-86.5 kcal/gfw
Lattice energy, U_0	184.2 kcal/gfw

It will be noticed that the calculation of lattice energy from experimental data gives a value which varies slightly from the one given in Table 4-3. Actually the theoretical value is probably more accurate than the experimental since the latter depends upon a somewhat questionable value for the electron affinity of the chlorine atom. In fact the most

reliable electron affinities are obtained by solving for them in Born-Haber series of equations in which theoretical values for lattice energies are used.

4-8 Solvation Energy. The interaction that takes place when a substance is introduced into a solvent is called *solvation*, and the energy change involved in this process may be denoted as the *solvation energy*. This definition is somewhat vague, but, in truth, the process by which a substance enters into a solution cannot always be given a clear-cut explanation. The topic of solvation is discussed more completely in connection with the problem of solubility (Sec. 6-4); at present we are interested only in the relation of this energy factor in the formation of the ionic bond.

Ionic and polar compounds (Sec. 4-16) are more soluble in polar solvents. The solubility of an ionic crystal is usually regarded as taking place because the polar-solvent molecules exert sufficient attraction for the ions to pull them away from their stations in the crystal lattice. However, the fact that many compounds are dissociated into ions in aqueous solution does not necessarily prove that all these substances must be constructed of ions in the solid state. Likewise it is incorrect to conclude that a substance which is insoluble in water must be nonionic in structure. In Sec. 4-5 it was suggested that the chemical union of two atoms produces an ionic bond when the difference between the ionization energy and electron affinity of the atoms of the two elements is not too great. Such a difference in energy, necessary to transfer the electron from one atom to another, may be supplied by the energy released when the ions take up their positions within the crystal, or covalent molecules, produced by interaction of two or more elements, may react with the solvent to yield ions. This latter reaction is necessarily exothermic, inasmuch as energy is supplied by the solvation process to complete the transformation from a covalent or polar bond to an ionic bond.

The physical properties of hydrogen chloride indicate that the compound is composed of molecules in which the atoms are held by a bonding that is largely covalent in character. Yet when hydrogen chloride is placed in aqueous solution, an acid is formed which is almost completely ionized, indicating that an interaction has taken place between the hydrogen molecules and the water molecules to produce hydrated chloride and hydronium ions. Since the ionization energy of the hydrogen atom is large and the electron affinity of the chlorine atom is comparatively small, the additional energy necessary to convert the covalent molecules into ions must be supplied by the solvation energy.

The ionization energy of the hydrogen atom is 312 kcal/gram atom, and the electron affinity of the chlorine atom is estimated to be 86.5 kcal/gram atom; therefore, when these two elements unite, it is to be expected that the resulting compound will be largely covalent unless the difference

of 225.5 kcal can be supplied by some other means to complete the transfer of the electron from the hydrogen atom to the chlorine atom.

The three possible energies of reaction between hydrogen and chlorine can be calculated as the sums of several thermochemical steps. The following series give approximately the energies of reaction involved in the formation of covalent hydrogen chloride, electrovalent hydrogen chloride, and finally the hydrated ions of these two elements:

$\frac{1}{2}\text{H}_2(g) \rightarrow \text{H}(g)$	51.6 kcal/gfw
$\frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Cl}(g)$	28.9 kcal/gfw
$\text{H}(g) + \text{Cl}(g) \rightarrow \text{HCl}(g)$	21.9 kcal/gfw
Energy of covalent $\text{HCl}(g)$	102.4 kcal/gfw
$\frac{1}{2}\text{H}_2(g) \rightarrow \text{H}(g)$	51.6 kcal/gfw
$\frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Cl}(g)$	28.9 kcal/gfw
$\text{H}(g) \rightarrow \text{H}^+(g) + e(g)$	312.0 kcal/gfw
$\text{Cl}(g) + e(g) \rightarrow \text{Cl}^-(g)$	- 86.5 kcal/gfw
Energy of electrovalent $\text{HCl}(g)$	306.0 kcal/gfw
$\text{H}^+(g) + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$	-256.0 kcal/gfw
$\text{Cl}^-(g) + x\text{H}_2\text{O} \rightarrow \text{Cl}(\text{H}_2\text{O})_x^-$	- 89.0 kcal/gfw
Solvation energy of electrovalent HCl	-345.0 kcal/gfw

The last two series of equations indicate that the solvation energy for the hypothetical electrovalent HCl is in excess ($345 - 306 = 39$ kcal/gfw) of the amount necessary to produce hydronium and chloride ions. Actually the two hydration energies cannot be obtained experimentally but must be calculated from other experimental values involving these two ions.

4.9. Ionic Radii and Crystal Structure. The binding force in the majority of inorganic crystals is predominantly ionic in character. Moreover, since coulombic forces are spatially undirected, the sizes of the ions are important factors in determining the structure of crystals. Numerous attempts have been made to calculate a reliable set of ionic radii, from which ionic distances might be estimated with a fair degree of accuracy. A discussion of these attempts is given in Sec. 3-17, and Table 3-15 lists values of ionic radii for some ions with inert gas configurations.

A crystal structure is largely determined by the ratio of the ionic radii of its components, and this ratio also regulates the coordination number of the smaller ion. In an ionic crystal each ion tends to surround itself with as many oppositely charged ions as possible, and the *number of nearest neighbors is the coordination number¹ of the central ion*. When two

¹ Not to be confused with coordination number used in a chemical sense in Chap. 5 to indicate the number of ions, atoms, or molecules grouped about a central metal ion in the formation of a coordination compound.

oppositely charged ions are brought together, they are attracted to each other by coulombic forces; but as they approach close to one another, the electrostatic force is counteracted by a repulsive force developed between the two electronic systems.) The ionic radii which have been assigned to ions from X-ray measurements are not actual radii but are instead the effective radii of the ions when packed together in a crystal. Ionic distances are always fractions of interionic distances and are so chosen that they may be used to predict other interionic distances in other crystals. It is usually assumed that the ions in a crystal are in bare contact with each other, but this assumption is not necessarily true. For convenience, ions are considered as rigid spheres; however, neither ions nor atoms have fixed surfaces, since the electron clouds of these particles may be constantly expanding and contracting and these clouds are certainly sometimes distorted by contact with other charged bodies.

The number of nearest neighbors is called the coordination number of an ion, and this number is dependent upon the radii of the ions, the radius ratio of the two ions, and the deformation of the ions as a result of size and charge. If we ignore the fact that ions may be deformed under the influence of surrounding ions, and if we consider them to be perfect spheres, it is possible to determine the geometric pattern formed by two different ions in a crystal which will satisfy both the spatial and coulombic-force requirements.

Assuming that ions are perfect spheres, it is possible to calculate, from geometrical considerations, the minimum radius of an ion around which other ions of unit radius can be arranged. In a substance of the general formula CA , if the ratio of the cation radius to the anion radius, r_c/r_A , is less than 0.15, then only two anions can be arranged about a cation so that the three ions are in contact. Similarly, if the ratio is greater than 0.15, only three anions may be in contact with one cation at the same time. If the ratio is greater than 0.22, only four anions at tetrahedral corners can touch one cation. For a ratio greater than 0.41 four anions may be arranged at the corners of a square, or six anions, at octahedral corners, can be in contact with one cation. When the ratio is greater than 0.73, only eight anions, at the corners of a cube, may be in contact with one cation. The first four postulated distributions of anions around a cation are shown diagrammatically in Fig. 4-1. The six hypothetical arrangements of ions within a crystal, calculated from radius-ratio rules, are given in Table 4-4. <

It has been customary to name each lattice type according to a familiar compound having that type of structure. For substances with the general formula CA the eightfold coordination is usually referred to as the *CsCl structure*, the sixfold coordination is called the *NaCl structure*, and the fourfold coordination is frequently denoted as the *zinc blende structure*,

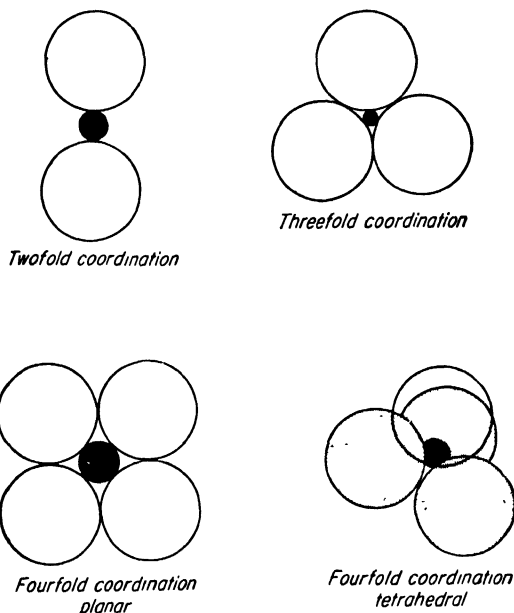


Fig. 4-1 Coordination number and the relative radii of ions.

although this latter compound is itself covalent. Of these three structures the first two are most common. In a crystal of the NaCl type each positive ion is surrounded by six negative ions arranged in an octahedron, and each negative ion is surrounded by six positive ions. Figure 4-2 shows the packing of the ions in sodium chloride, and Fig. 4-3 indicates the pattern in a unit cell of the sodium chloride structure.

A lattice is considered as being indefinite in extent and constructed of an infinite repetition of a small group of ions, the latter constituting an imaginary *unit cell*. This unit is the smallest portion of the crystal

TABLE 4-4 HYPOTHETICAL ARRANGEMENTS OF ANIONS ABOUT A CATION AS CALCULATED FROM RADIUS-RATIO RULES

Coordination number (number of anions)	Geometric arrangement in crystal	Radius ratio, r_c/r_a
2	Linear	Up to 0.15
3	Triangular	0.15–0.22
4	Tetrahedral	0.22–0.41
4	Planar	0.41–0.73
6	Octahedral	0.41–0.73
8	Cubic	0.73 and above

lattice which possesses all the various kinds of symmetry which characterize the crystal. Actually it is not possible for a single unit cell to exist alone, since the boundaries of the unit cell are also the boundaries of neighboring unit cells.

As indicated in Fig. 4-2, the radii of sodium ions are less than the radii of chloride ions, and the sizes of the ions play a most important role in determining the lattice structure. Geometrically a crystal structure is as compact as the effective radii of the ions will permit, while at the same time keeping similar ions more or less separated by means of a region

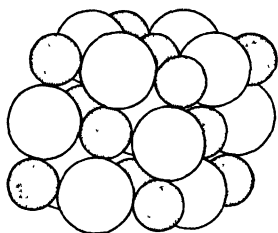


Fig. 4-2 The packing of the ions in sodium chloride; the small spheres represent sodium ions and the large spheres chloride ions.

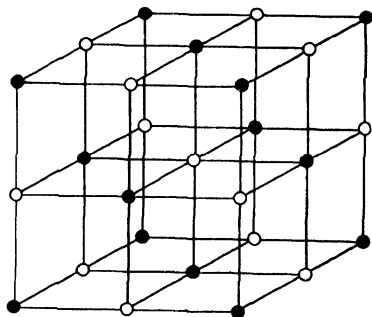


Fig. 4-3 The crystal pattern of sodium chloride.

that is occupied by ions of opposite charge. If we examine Fig. 4-3 in respect to the sodium ions only, they are found to be located at the corners of a cube, with another sodium ion stationed in the center of each of its faces. A crystal pattern of this type is known as the *face-centered cubic lattice*.

The ratio of the ionic radii in the sodium chloride lattice is approximately 0.53, and this value indicates that the radius of the sodium ion is about one-half that of the chloride ion. In cesium chloride the ratio of ionic radii is about 0.93; therefore the radii of the two ions are nearly equal. Since the radius ratio is different from that in sodium chloride, it is to be expected that the packing pattern within the crystal will be different. To produce close packing in CsCl , eight ions of one type are arranged symmetrically about an ion of opposite charge. Figure 4-4 shows the packing pattern in a unit cell of cesium chloride. This method of packing produces an arrangement which is known as a *body-centered cubic lattice*. This descriptive term arises from the fact that each cesium ion may be considered as being the center of a cube whose eight corners are occupied by chloride ions. Likewise each chloride may be regarded

180 Fundamental Concepts of Inorganic Chemistry

as occupying the center of a cube on whose corners are stationed eight cesium ions. Figure 4.5 is a diagrammatic representation of a unit cell of the cesium chloride structure.

The concept of ions acting as perfect spheres and arranging themselves in definite crystal patterns is not sufficient to account for the crystal

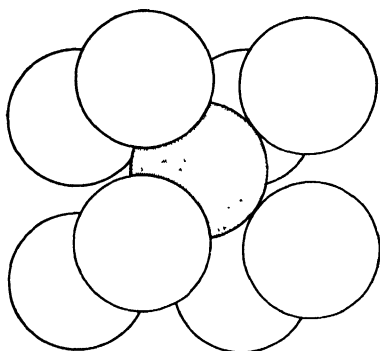


Fig. 4.4 The arrangement of ions in cesium chloride.

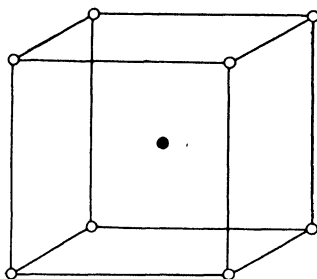


Fig. 4.5 A unit cell of the cesium chloride structure.

structure of all ionic substances. There are crystal lattices in which the ions do not behave as true spheres. In these crystals the ionic radii do not add to give the internuclear distance between ions as measured by X-ray analysis. Such discrepancies are believed to result from a distortion or polarization of one or more ions within the lattice. The electron cloud of a large ion is relatively far removed from the nucleus. An adjacent ion of opposite charge may distort a loosely held electron cloud in such a manner as to produce an unequal distribution of electric charge

TABLE 4.5 CLASSIFICATION OF SPACE LATTICES

Crystal systems	Lattice types	Examples
Cubic	Simple cube; face-centered cube; body-centered	CaO, CsCl, NaCl, Ni-(NH ₃) ₆ Cl ₂
Tetragonal. . . .	Tetragonal prism; body-centered tetragonal prism	SnO ₂ , K ₂ PtCl ₆ , BaSO ₄ ·4H ₂ O
Orthorhombic. .	Rectangular prism; body-centered rectangular prism; rhombic prism; body-centered rhombic prism	HgCl ₂ , K ₂ SO ₄
Monoclinic. . . .	Monoclinic parallelepiped; monoclinic one-face centered	KClO ₃ , K ₃ Fe(CN) ₆ , CaSO ₄ ·2H ₂ O
Triclinic	Triclinic parallelepiped	CuSO ₄ ·5H ₂ O, K ₂ S ₂ O ₈
Hexagonal.	Hexagonal prism	SiO ₂ (quartz), AgI
Rhombohedral.	Rhombohedron	Al ₂ O ₃ , CaCO ₃ (calcite)

on the larger ion. As a general rule, distortion or polarization is greater for negative ions than for positive ions, because the former are much larger. This polarization becomes appreciable for the anions of large radius, as, for example, the sulfide and iodide ions. In lattices containing these ions polarization may have the effect of pulling the ions into the form of sheets, in such a way that the distorted ions are no longer symmetrically surrounded by ions of opposite charge. A crystal structure of this type is known as a *layer lattice*, and in a succession of layers the

TABLE 4-6 THE SEVEN CRYSTAL SYSTEMS

System	Essential symmetry	Axes* in unit cell	Angles* in unit cell
Cubic	Four threefold axes	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	One fourfold axis	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	Three mutually perpendicular twofold axes, or two planes intersecting in a twofold axis	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	One twofold axis, or one plane of symmetry	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$
Triclinic	No planes, no axes	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$
Hexagonal	One sixfold axis	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
Rhombohedral	One threefold axis	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

* The axes lie along coordinates in space; α , β , and γ are the angles between the three axes of the crystal, and a , b , and c are the lengths of the axes.

ions are arranged as $+ - - + - - +$, etc. The arrangement in the cadmium iodide lattice is a typical example of a layer structure.

The foregoing discussion of ionic crystals is quite incomplete and greatly oversimplified. It is beyond the scope of this book to deal with the subject of crystal chemistry. However, to complete the present condensation of this subject, it should be pointed out that, although we have mentioned only a few types of crystal lattices, many others exist (Sec. 4-19). In all, 14 types of unit cells are possible, which determine the different forms of symmetry found in the seven crystal systems. The various possibilities are summarized in Tables 4-5 and 4-6, and the arrangements of ions in the several unit cells are indicated in Figs. 4-6 and 4-7.

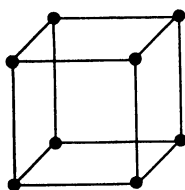
4-19 Some Physical Properties of Ionic Compounds. The type of bond occurring within a given compound cannot always be predicted from its crystal structure. It is true, however, that the crystal pattern may indicate the presence of a certain bond type. For example, the NaCl crystal structure does not permit the formation of covalent bonds,

182 Fundamental Concepts of Inorganic Chemistry

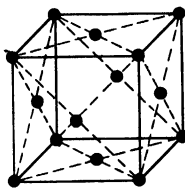
because there are too many neighbors grouped around the sodium ion to allow each one to be held by an electron pair. On the other hand there are comparatively few inorganic crystals which are either 100 per cent ionic or 100 per cent covalent. The majority of crystals are held together by bonds which are partly ionic and partly covalent.

CUBIC

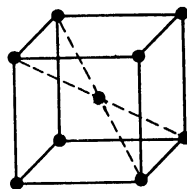
Three equal axes at right angles



Simple



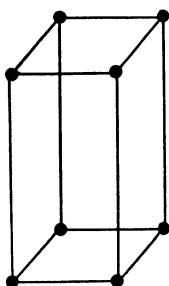
Face-centered



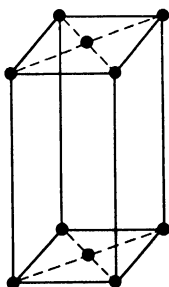
Body-centered

ORTHORHOMBIC

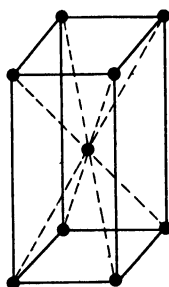
Three unequal axes at right angles



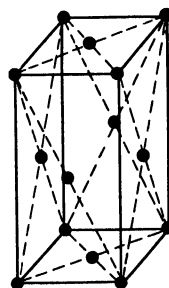
Simple



End face-centered



Body-centered



Face-centered

Fig. 4-6 Unit cells in cubic and orthorhombic crystal systems.

Although the occurrence of pure ionic bonding is rare, a sufficient number of largely electrovalent compounds exist so that it is possible to make certain generalizations in regard to the physical properties that these substances might be expected to possess. As a general rule, typical ionic crystals are hard and have high melting and boiling points. These properties are related to the size of the ions and their electronic configurations. Hardness seems to increase fairly regularly as the interionic distance decreases. When the distance between the effective charges on the ions is short, the electrostatic attraction between the ions is strong; there-

fore small ions would be expected to form hard crystals. Likewise, to split an ionic crystal it is necessary to overcome these coulombic forces between ions. Furthermore such crystals are neither malleable nor plastic, since the sliding of one layer of ions over another would bring

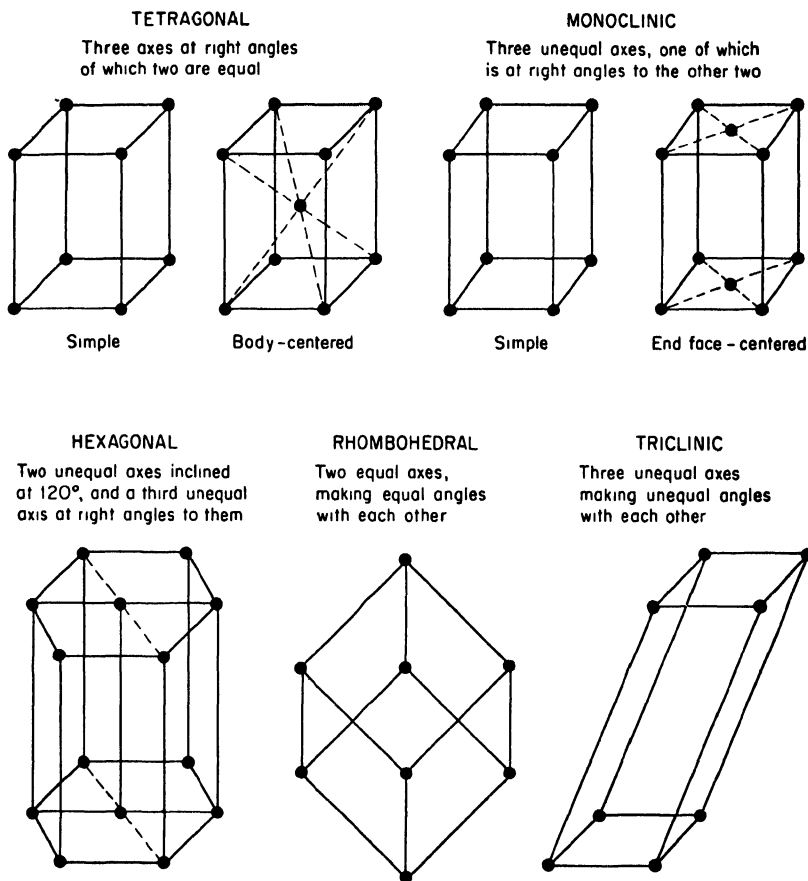


Fig. 4-7 Unit cells in tetragonal, monoclinic, hexagonal, rhomboidal, and triclinic crystal systems.

together like charges, which, because of their repulsion to each other, would result in a rupture of the crystal. Also, ions bearing multiple electric charges, such as Ca^{++} , Al^{3+} , SO_4^{-} , and PO_4^{3-} , give rise to very strong attractive forces and, in the absence of ionic deformations, form hard crystal structures.

Hardness is usually measured according to Mohs' scale, which classifies

184 Fundamental Concepts of Inorganic Chemistry

a substance according to whether or not it can be scratched by certain standard substances. The relation of hardness to charge on, and distance between, ions is indicated in Table 4-7.

TABLE 4-7 RELATION OF HARDNESS TO IONIC CHARGE AND INTERIONIC DISTANCE

Compound	Hardness according to Mohs' scale	Interionic distance, Å
BeO	9.0	1.65
MgO	6.5	2.10
CaO	4.5	2.40
SrO	3.5	2.57
BaO	3.3	2.77
NaF	3.2	2.13
MgO	6.5	2.10
ScN	7.9	2.22
TiC	8.9	2.16

Although great hardness is to be expected in crystals composed of small ions with high charges, the converse conclusion that hard substances are composed of ions is not necessarily true. For example, diamond, the hardest of substances, is not composed of quadrivalent negative and positive ions of carbon. Neither is carborundum built up of oppositely charged ions of silicon and carbon. The components of both diamond and carborundum lattices are held by covalent bonding, indicating that under certain conditions atomic bonding may produce crystals as hard as or harder than ionic crystals.

We have said that hardness seems to increase somewhat regularly as interionic distances decrease. The same relation does not necessarily exist between melting point and interionic distance. In fact inorganic substances with the highest melting points contain the largest cations. This statement is borne out by the melting points of a series of the fluorides which are tabulated in Table 4-8.

TABLE 4-8 THE MELTING POINTS, DEGREES CENTIGRADE, OF A SERIES OF ELEMENTS AS FLUORIDES

Compound.....	NaF	MgF ₂	AlF ₃	SiF ₄	PF ₅	SF ₆	IF ₇
Melting point.....	992	1396	1040	-77	-83	-56	5.5

Melting points of crystals with ionic characteristics are related to the coordination number of the crystal structure. In Table 4-8 the wide change in melting point between AlF₃ and SiF₄ is frequently attributed incorrectly to the transition from ionic bonding to atomic bonding. It is

true that fluorides of Si, P, S, and I are molecular crystals and that those of Na, Mg, and Al form crystals with ionic patterns, but it is doubtful that the transition in melting points between AlF_3 and SiF_4 represents a similar rapid transition in bond types. The relative sizes of the aluminum and fluoride ions are such that the coordination number of the aluminum ion in aluminum fluoride is 6. Therefore every fluoride ion must be attached to two aluminum ions in order to attain the chemical ratio of $\text{Al}/3\text{F}$. This is possible only in a crystal pattern of indefinite extent with an infinite number of aluminum and fluoride ions. On the other hand the silicon ion is only large enough to accommodate four neighbors. Consequently the coordination number and the valence number are the same, and each fluoride ion in SiF_4 can belong to only one silicon ion. This instance of coordination number and valency being the same, as in a molecule of SiF_4 , where a unit cell is composed of four fluoride ions around one silicon ion, results in an electrically neutral complex. Therefore a particle of SiF_4 behaves like a molecule, and the forces extending from it are weak, producing a type of bonding known as *van der Waals interaction* (Sec. 4·26).

Electrovalent bonding produces crystals which are very poor conductors. This statement holds true when these substances are in a solid state. Near the melting point or in a molten condition such substances become good conductors. The increased conductivity is related to the destruction of the crystal lattice. At or near the melting point of an ionic crystal sufficient energy has been added to be equivalent to that released when the crystal was formed. Consequently an ionic compound in a molten state is composed of ions which are not restricted to relative stationary positions as in a lattice. The freely moving ions permit electric conductance; hence there is a transfer of material when fused crystals are subjected to electrolysis.

Ionic crystals resist compression, and this resistance is directly related to hardness and the interionic distances within the crystal structure. Where the interionic distances are large, some compression may be expected but in a closely knit structure little compression can be anticipated.

Ionic compounds are more soluble in polar solvents. The problem of solubility is considered in more detail in Chap. 6, but at present it is pertinent to state that this property is related to the stability of the crystal involved. A salt dissolves in water when the interaction between the ions in the lattice and the dipoles (Sec. 4·24) of the water molecules is energetically sufficient to overcome the coulombic forces holding the ions in the lattice. In other words, when the energy of hydration is greater than the lattice energy, a substance should be soluble in water.

The transition from ionic to covalent bonding in a series of related com-

186 Fundamental Concepts of Inorganic Chemistry

pounds frequently appears to be more abrupt than actually occurs. The sudden change in melting point among the fluorides listed in Table 4-8 is explained as being a change in the coordination number of the ions within the substances. Nevertheless, there is a transition of bond types among cation compounds in passing from left to right in the Group A elements of the Mendeleev periodic table. Regardless of the true explanation for rapid transitions in bond types there exists a sharp demarcation between what are apparently ionic and covalent chlorides, as is evidenced by a comparison of the fusibility, volatility, and equivalent conductivity of the molten compounds. As indicated by these physical properties, the metallic chlorides may be classified unambiguously into either true salts or covalent compounds. Such a division is indicated in Table 4-9.

TABLE 4-9 TRUE SALTS AND COVALENT CHLORIDES*

	HCl			
Melting point, °C	-114			
Boiling point, °C	-85			
Equivalent conductance†	10 ⁻⁶			
	LiCl	BeCl ₂	BCl ₃	CCl ₄
Melting point, °C	606	404	-107	-23
Boiling point, °C	1337	500	12 6	77
Equivalent conductance	166	0 086	0	0
	NaCl	MgCl ₂	AlCl ₃	SiCl ₄
Melting point, °C	800	718	..	-70
Boiling point, °C	1442	1000	183	58
Equivalent conductance	134	29	1 5 × 10 ⁻⁵	0
	KCl	CaCl ₂	GaCl ₃	GeCl ₄
Melting point, °C	768	774	75.5	-50
Boiling point, °C	1415	1100	205	87
Equivalent conductance	104	52	10 ⁻⁷	0
	RbCl	SrCl ₂	InCl ₃	SnCl ₄
Melting point, °C	717	870	586	-30
Boiling point, °C	1388	1250		114
Equivalent conductance	78	56	15	0
	CsCl	BaCl ₂	TlCl ₃	PbCl ₄
Melting point, °C	645	960	25	-15
Boiling point, °C	1289	1350	100	105 d.
Equivalent conductance	67	65	10 ⁻³	2 × 10 ⁻⁵

* The heavy line marks the division between electrovalent and covalent chlorides as reflected in each of the properties cited.

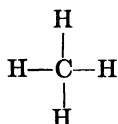
† Equivalent conductance is for the molten compound at its melting point.

THE COVALENT BOND

A qualitative discussion of the ionic bond presents little difficulty for the student. He is familiar with the laws of electrostatics from an

elementary study of physics; therefore, with the relatively simple mathematics involved in a qualitative approach, the idea of different sizes of ions with opposite charges being packed in a crystal lattice is grasped easily enough. The same cannot be said for the explanation of covalency. Almost any analytical treatment of the covalent bond is a more difficult problem than is the analysis of electrovalency. A quantitative approach to the problem of the shared bond requires the use of the mathematics of wave mechanics. Even a qualitative discussion is more or less ineffectual when presented in a nonmathematical manner.

In the nineteenth century valence bonds between atoms in a molecule such as methane were represented by single lines joining the chemical symbols of the chemical elements in the compound. The symbolism used to represent a molecule like methane



expressed certain chemical facts but had little significance with regard to molecular structure. The discovery of the electron in the early part of the twentieth century stimulated many attempts toward the formulation of an electronic theory for valency. These efforts culminated in the work of G. N. Lewis, who, in 1916, introduced the idea of the *electron-pair bond*, or covalent bond (Sec. 4·2). He called attention to the fact that most compounds contain an even number of electrons and emphasized the tendency of combining atoms to fill up a shell of eight electrons. At that time the so-called rule of eight was quite compatible with the classical valence-bond concept which had been so successful for nearly a century in explaining the chemical structure of organic compounds. Although the Lewis theory of valency stressed the tendency of reacting atoms to attain the structure of inert gas, it offered no reason why such a structure was stable. It also gave no explanation as to why a shared electron pair constituted a stable chemical bond. In other words, the Lewis explanation of electronic structure fitted fairly well into observed facts, but it offered no real understanding of the nature of chemical bonding.

Within recent years two main approaches have been developed in the application of wave mechanics to the electrons involved in chemical bonding. The first of these, advanced by Heitler and London in 1927 and later extended by Pauling and Slater in 1931, is based upon the pairing and neutralization of opposed electron spins. The Pauling-Slater extension of this theory accounts for the directional characteristics of

covalent bonds. This theory is generally designated as the *valence-bond approach*. The second means of applying wave mechanics to those electrons comprising a covalent bond was developed by Hund, Mulliken, and Lennard-Jones and is known as the *method of molecular orbitals*. The latter approach derives its name from the fact that it discards the concept of atomic orbitals and assumes instead that the molecule as a whole

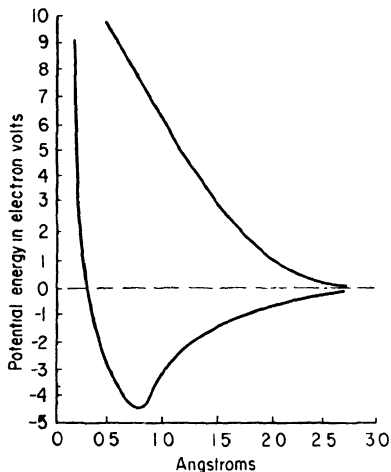


Fig. 4-8 Energy of two interacting hydrogen atoms as a function of internuclear distance. The lower curve is for atoms with opposed spins, and the upper curve is for atoms with parallel spins.

steps, the interaction between the particles ranges from no reaction at a relatively great distance to one producing a large repulsive force when the two positively charged nuclei are forced closely together. Between these two extremes there is a short-range distance through which occurs the interaction that develops the potential energy of the covalent bond. In Fig. 4-8 the lower curve shows the potential energy of interaction for two normal hydrogen atoms of opposed spins. The problem is to explain the minimum in this curve, which represents the optimum distance between atoms, and the maximum potential energy developed in the bonding of the two hydrogen atoms.

The answer to this problem, in terms of quantum mechanics, may be obtained by solving the Schrödinger equation (Sec. 2-29) for the system of two electrons and two protons. Without undertaking a solution of Schrödinger's equation, we can say that there is a definite distance between the two hydrogen nuclei where an interaction arises due to the wave

has definite electronic levels corresponding to those in an atom.

4-11 The Valence-bond Approach to Molecular Structure.

The simplest example of a stable covalent compound is the hydrogen molecule. The electronic structure for this molecule is written $H:H$, indicating that the two electrons are shared between the two atoms and form the bond between them. This bond is quite strong, as shown by its dissociation energy of 103.2 kcal/gfw. The question then arises as to how it is possible for two neutral atoms, of similar structure, to combine and to form a stable molecule containing the same two atoms.

If it is assumed that two atoms of hydrogen, designated as A and B , are brought together in a series of

nature (Sec. 2-27) of the two electrons belonging to the two atoms. As a result of the wave nature of an electron its position cannot be confined to any localized orbit. Instead there is a probability of the wave particle being found elsewhere in space. However, a valence electron, acting as a wave, operates effectively only over a distance of atomic dimensions. Within this range the two electrons of atoms *A* and *B* are no longer identified with their original nuclei. Each electron has an equal probability of being found on either atom, and each nucleus may be associated with both electrons. The exchange of electrons between nuclei is to be considered not as a juggling act of particles but as a condition where the wave motions of the electrons overlap so that they may belong equally to both nuclei.

In addition to the properties of mass, electric charge, and wave motion the electron has associated with it other properties which are related to its spin (Sec. 2-23). It may seem contradictory to speak of the wave motion of an electron and then describe it as spinning about its own axis similar to a top. However, a fast-moving top may have a blurred position even though the direction of its spinning motion is known. Furthermore the direction of spin is a determining factor in bond formation. As a result of its spin the electron possesses a magnetic dipole (Sec. 4-24) which causes it to behave as if it were a small magnet. When two electrons of opposite spins come within atomic distances of each other, the mutual neutralization of their dipole moments results in an attractive force between the two particles. Conversely the magnetic moments of two electrons with parallel spins oppose each other, and their approach brings a repulsive force into play. A stable bond between two hydrogen atoms can be formed only when the spins of the two electrons are opposed.

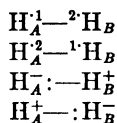
The Pauli exclusion principle (Sec. 2-24) states that only two electrons may occupy the same orbital and two such electrons must have opposed spins. When two hydrogen atoms are brought within bonding distance of each other, the operation of Pauli's exclusion principle takes over. If the spins of the two electrons are in the same direction (parallel), both electrons can be accommodated only if one electron is promoted (excited) to a higher quantum ($2s$) state. This promotion requires energy, and the potential energy of such a hypothetical molecule would be higher than that of the separate hydrogen atoms. Consequently, when two atoms with electrons of parallel spins are brought together, their approach produces sufficient repulsion to prevent the formation of the covalent bond (see upper curve, Fig. 4-8).

To attempt a word description of the forces which make up the covalent bond is undoubtedly foolhardy; nevertheless, without undertaking a mathematical analysis, some sort of picture seems necessary. We ven-

ture to suggest that the forces operating in this bond are largely electrostatic. Such forces are the same as those which operate in an atom to hold electrons to a nucleus, except that in the case of covalent bonding there is a change in electron densities in the combining atoms. The bond is the result of an accumulation of electron densities. To be more specific, when two atoms approach within atomic distances of each other, two valence electrons with opposed spins can exhibit their property of wave motion and produce an overlapping of waves. This overlapping of electron waves, arising from the wave nature of the electrons, causes an increase in electron density wherever the overlapping occurs. It may be assumed that the maximum density will accumulate at the mid-point between the two atoms. Thus a large part of the binding force of the covalent bond may be considered as resulting from the electrostatic attraction of the nuclei for the accumulated electron cloud between them.

The covalent bond is formed between atoms that share a pair of electrons with opposite spins. In the case of the hydrogen molecule the dissociation energy of the bond (the amount of energy necessary to separate the two hydrogen atoms) is 103.2 kcal/gfw. It may be concluded that an equivalent amount of energy is released when the bond is formed. In other words, the potential energy of the hydrogen molecule is less than that of its two separate atoms. The release of energy comes from two sources: the neutralization of the spin magnetic moments of the two electrons, and the accumulation of electron density between the two atoms.

4.12 The Concept of Resonance. The discussion given in the preceding section is only one of many possible explanations of what happens in the process of forming a covalent bond. Many authors attribute the establishment of this bond and the resulting release of energy to the formation of a *resonating* molecular structure. The term *resonance* is misleading in that it does not imply any juggling of electrons or oscillations between various electronic structures. Instead it is used to describe, or designate, the configuration of a molecule that is a hybrid of other electronic structures. Thus, for any system of two or more possible structures, the true structure is neither one of the possibilities nor an average of all of them but is instead a hybrid that defies pictorial representation. The *resonance hybrid* is that structure which imparts maximum stability to the system and is, consequently, the structure possessing the lowest energy state. As an example of what is meant by a resonance hybrid, consider the formation of the hydrogen molecule. If the hydrogen atoms are designated as *A* and *B* and their electrons as 1 and 2, then, because of the uncertainty principle in regard to the locations of the two electrons, it is possible to have at least four possible electronic structures. Four of these electronic structures can be written as



However, none of the four possible structures represent the true structure of the hydrogen molecule. Also, the actual structure cannot be represented as an average of any or all of the above structures. The real picture of the hydrogen molecule cannot be represented because it is a hybrid of all the above structures. Furthermore it possesses a lower energy state than any of the four configurations. In the formation of a resonance structure or a resonating bond with maximum stability and lowered energy state, it is necessary that energy be released in the process. The energy so released is sometimes referred to as *resonance energy*, or less frequently as *exchange energy*.

4.13 Directed Bonds. According to the interpretation offered by the Heitler-London theory, the covalent bond between two atoms, consisting of an electron pair, is produced by the overlapping of the wave functions of the two electrons with opposite spins. The accumulation of negative charge between the two atomic nuclei results in an electrostatic attraction between the nuclei and the piled-up charge. However, this theory offered no explanation for the directional characteristics of the covalent bond. It was Pauling who first suggested that bonding will take place in such a manner that the overlapping of wave functions will be a maximum. Inasmuch as the wave functions of certain orbits are directional, it follows that bonding involving electrons in these orbits should also be directed in space.

Pauling and Slater, accepting the essential details of the Heitler-London theory, have developed an extension to account for the directional nature which may occur in the covalent bond. (According to the Pauling-Slater theory the greater the overlap of wave functions, the stronger is the bond that is formed. With this theory certain rules have evolved concerning bond formation. The atomic orbitals of two electrons making up a covalent bond will tend to overlap with each other but will avoid overlapping with the electrons of other atoms. Consequently a nonspherical orbital will tend to form a bond in the direction of greatest electron concentration within the orbital. Furthermore an orbital which is concentrated in one direction will tend to form stronger bonds than another orbital of similar stability but less directionally concentrated.)

(The distributions of charge intensities of electrons are geometrical in character, and the spatial symmetry which may be expected depends upon the orbit in which the electron occurs.) (The wave function of an electron in an *s* orbital is spherically symmetrical; therefore such an elec-

tron exhibits no directional preference in bond formation. However where p and other orbitals are involved in bonding, it is assumed that since the orbitals are directional, the bonds will likewise have spatial direction. Experimental evidence supports this assumption. (The three p orbitals with wave functions p_x , p_y , and p_z are theoretically directed along three axes, and the electron densities are dumbbell-shaped when the orbits are occupied by electrons.) Polar graphs of the s and p orbitals are indicated in Fig. 4-9.

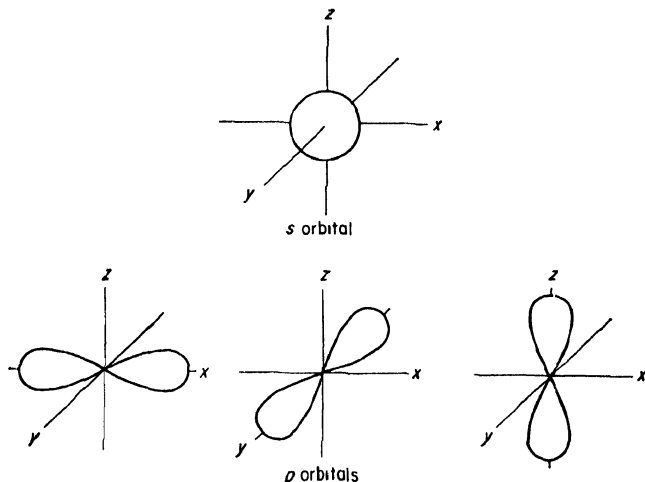


Fig. 4-9 Polar representation of the s and p orbitals.

(The distribution of electrons in an atom with incomplete p and d orbitals follows an empirical *rule of maximum multiplicity*, which states that, when electrons are added successively, as many orbitals are singly occupied as possible before any pairing of electron spins occurs. The oxygen atom has the structure $1s^2 2s^2 2p^4$, or, better still, $1s^2 2s^2 2p^2 2p^1 2p^1$, indicating that all three p orbitals are tenanted, but only one is complete with two coupled electrons, whereas the other two p orbitals are singly occupied. Consequently the oxygen atom has a valence of 2, because the two unneutralized spins of electrons in the two singly occupied orbitals may be coupled with two other unneutralized electron spins in other atoms. When the oxygen atom combines with two hydrogen atoms to form a molecule of water, the two OH bonds should be at right angles. Figure 4-10 is a diagrammatic representation of the directed bonds in the water molecule. In like manner the nitrogen atom with the structure $1s^2 2s^2 2p^1 2p^1 2p^1$, containing three unpaired $2p$ electrons, will combine with three hydrogen atoms to form a molecule of ammonia with

a pyramidal structure. This structure is indicated in Fig. 4-11. The diagrams in Fig. 4-10 and 4-11 indicate that the directed bonds in water and ammonia, falling along the cartesian axes, should form 90° angles with each other. Actually the angles are greater, being 105° for water and 108° for ammonia. The distortion¹ from a right angle in either case is attributed to repulsive forces between the hydrogen atoms.)

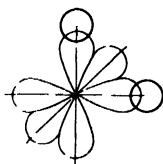


Fig. 4-10 Diagrammatic representations of the directed bonds in the water molecule.

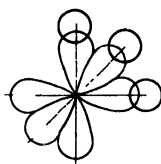
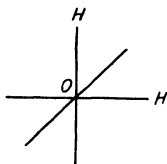


Fig. 4-11 Diagrammatic representations of the directed bonds in the ammonia molecule.

4-14 Hybrid-bond Orbitals. The stereochemistry of beryllium, boron, carbon, and many other elements cannot be explained so simply as were the structures for oxygen and nitrogen in the water and ammonia molecules. Because of its wide range of compounds the case of carbon is most interesting. (The carbon atom has only two unpaired electrons in its ground state, and, with an electronic configuration of $1s^2 2s^2 2p^1 2p^1$, one would expect it to be capable of forming two covalent bonds. However, the divalent compounds of carbon are not nearly so important as are the tetravalent compounds. To explain this anomaly, one must speculate as to how carbon may attain four unpaired electrons. This tetravalency can be gained by exciting one of the $2s$ electrons to the third $2p$ state with the resulting configuration of $1s^2 2s^1 2p^1 2p^1 2p^1$. With this electronic distribution it would be expected that the three p electron clouds would be oriented at right angles, as in ammonia, and that the s electron clouds should be angled in whichever direction is sterically convenient. Furthermore it might be presumed that the three dumbbell-shaped p electron clouds would form the three strongest bonds and that the one spherical s electron might form a weaker bond.

Experimental evidence shows that the four carbon bonds are of equal strength. The mathematics of wave mechanics has also demonstrated that the most stable bonds are not necessarily formed from p electron clouds but that a reshuffling of wave functions may produce what are known as *hybrid orbitals*.) According to the quantum-mechanical treatment the wave functions of the carbon-atom electrons are hybridized in such manner that there is a redistribution of electron densities. The end

¹ Another explanation attributes the distortion in the water molecule to the tetrahedral hybridization of the oxygen orbitals (Sec. 4-14).

194 Fundamental Concepts of Inorganic Chemistry

result is four new electron clouds which are mutually equivalent to each other. The equivalence of the carbon valencies produces the four strongest possible bonds and accounts for the fact that these four bonds point to the corners of a regular tetrahedron, making an angle of $109^{\circ}28'$ with each other. A diagram indicating the tetrahedral structure of methane is given in Fig. 4-12.

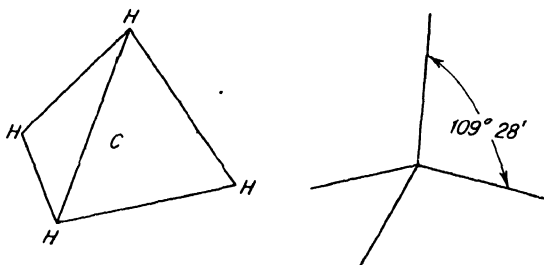


Fig. 4-12 The tetrahedral structure of the methane molecule, and the directed valencies of carbon.

(In the case of the carbon atom the reshuffling of wave functions is called *s-p hybridization*, since the actual bonds are formed by combining s^+ and p^- functions to produce stronger bonds than either separately. However, hybridization is possible with other sets of orbitals. In fact the majority of covalent bonds are produced from hybridized orbitals. Examples of such hybridized orbitals are to be found in many of the compounds of the transition elements. In these elements the *d* orbitals are only slightly more stable than the outer *s* level; consequently it is possible to have *d-s-p hybridization* in the filling of the outer orbitals (Sec. 5-5). The most common types of hybridization, together with the spatial arrangements of the bonds about the central atom, are given in Table 4-10.

TABLE 4-10 DIRECTIONAL CHARACTERISTICS OF SOME COVALENT BONDS

Coordination number	Hybrid-bond type	Spatial arrangement*	Examples
2	sp	Linear	$\text{Ag}(\text{CN})_2^-$
3	sp^2	Triangular, planar at 120°	BBr_3
4	sp^3	To the corners of a tetrahedron	CH_4
4	dsp^2	Square, planar at 90°	$\text{Ni}(\text{CN})_4^-$
6	d^2sp^3	To the corners of an octahedron	$\text{Co}(\text{CN})_6^{3-}$

* Coordination number in these spatial arrangements is used in a chemical sense, and not according to the physical interpretation described in Sec. 4-9.

4-15 Molecular Orbital Approach to Molecular Structure. In our consideration of atomic structure the assumption was made that, in the process of atom building, electrons are added to certain restricted orbitals within successive higher energy levels until the electronic configuration of the particular element is attained. The molecular orbital method attacks the problem of molecular structure in a similar fashion. In this approach it is assumed that there are definite electronic levels within a molecule which correspond to those in an atom. Furthermore a molecule may be regarded as the result of adding electrons, one by one, into a system of nuclei until definite molecular orbitals within successive higher energy levels are filled.

The principal difference between the atomic and molecular structure is that molecules do not have the possibilities of symmetry that characterize atomic electron clouds. Where atoms possess spherical symmetry, molecules are limited to cylindrical symmetry and in some molecules no symmetry is possible. Because of this difference in symmetry the principal and subordinate quantum numbers n and l , in molecules, do not have the same significance as in atomic structure. For diatomic molecules the molecular quantum numbers include a principal quantum number, n , and a quantum number, λ , which describe the components of angular momentum along the axis joining the atomic centers. An atom has no axis of this kind. If we visualize a diatomic molecule as being cylindrical in shape with an axis lying between the two nuclei, then n will denote the energy level (roughly the distance from the axis) and λ is the quantum number which measures the number of units of angular momentum of the electronic orbital motion projected along the axis. Therefore λ takes the place of the atomic quantum number l .

Just as the letters s , p , and d are used to designate the shapes of electron orbits in atoms, where $l = 0, 1$, or 2 , so are the Greek symbols σ , π , and δ used to describe the electrons in molecules, where $\lambda = 0, +1$, or $+2$. For molecules in which two nuclei have moved up close to one another, the same shells may be assumed as for the atoms. As electrons are added successively into the molecular orbitals, a series of closed groups are built up in a manner similar to the building of closed shells in the outer structure of an atom. In accordance with the Pauli principle electrons enter into molecular orbitals with their spins either paired or single, but pairing does not occur until after a given electronic group is half filled.

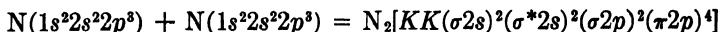
In the formation of molecules interaction occurs between the electrons originating from the individual atoms. If, as a result of lack of accommodation, an electron is forced to occupy in the molecule a principal quantum level higher than that in the atom from which it originated, the electron is said to be *promoted*. Such a promotion requires a large amount of energy; therefore the presence of promoted electrons confers

instability on the molecule. Electrons which have been excited to a higher energy level are called *antibonding*, since the energy of promotion is translated into forces of repulsion. When electrons have a lower potential energy in the molecule than in the original atom, they are called *bonding electrons* and the energy released is converted into forces of attraction between coupled electrons. As might be expected, the presence of bonding electrons confers stability upon the molecule. Electrons in completely closed shells (that is, *K* and *L* shells) of atoms are practically unaffected when the atoms are brought together to form the molecule. Electrons so described are treated as *nonbonding electrons*. Since a molecule can be formed only when the total energy of the system decreases, the number of bonding electrons must exceed the number of antibonding electrons. As a general rule, one-half the difference between the number of bonding and antibonding electrons indicates the probable number of electron-pair bonds in the molecule.

When two reacting atoms are brought together to form a molecule, an interaction occurs between the electrons from the individual atoms whereby the structure of the molecule is stabilized. This interaction produces three electron combinations, known as σ , π , and δ bonds, and the electrons which form the bonding are designated by the same Greek symbols. In σ bonding the charge distribution has cylindrical symmetry about the axis joining the two nuclei. This is not true for π and δ bonding. Since an *s* electron in an isolated atom has spherical symmetry, it will have zero orbital angular momentum along the internuclear axis of the molecule. In this case λ is zero, and the electron becomes a σ electron. For a *p* electron λ may be $+1$, 0 , or -1 , depending upon its angular momentum along the line joining the two atoms; therefore it may become either a σ or a π electron in the molecular orbital. Of the six *p* electrons, the maximum number possible in a shell, the first two produce a σ bond, and the other four enter into π bonding. In the case of the ten possible *d* electrons two may enter into σ bonding, four into π bonding, and four into δ bonding. Thus each group of two σ , four π , and four δ electrons constitutes a closed energy level. Any additional electrons must be placed in the next higher energy level. The foregoing process is summarized in Table 4-11.

The qualitative application of the molecular orbital method may be illustrated by giving an oversimplified explanation of the formation of the nitrogen molecule. This particular molecule must be formed by the union of two atoms each having the configuration of $1s^2 2s^2 2p^3$. Furthermore it may be assumed that the *s* electrons in the *K* shells are nonbonding and may be disregarded for the sake of simplicity. This leaves the two *s* and three *p* electrons in the incomplete *L* shells of the two atoms to

be considered in the bonding interactions. The formation of N_2 proceeds according to the following equation:



The KK symbols indicate the K shells containing the nonbonding electrons. Of the four $2s$ electrons in the two atoms, two become $\sigma 2s$ electrons, which are bonding electrons, and two become $\sigma^* 2s$, which are promoted and are therefore antibonding. The six p electrons interact to form two $\sigma 2p$ and four $\pi 2p$ electrons, all of which have a lower potential in the molecule than in the isolated atoms and, consequently, are bonding

TABLE 4-11 CORRELATION BETWEEN ATOMIC AND MOLECULAR ORBITALS

Complete electron groups in isolated atoms	Values of l	Possible values for λ	Complete electron groups in molecules
s^2	0	0	σ^2
p^4	1	0, ± 1	σ^2, π^4
d^{10}	2	0, $\pm 1, \pm 2$	$\sigma^2, \pi^4, \delta^4$

electrons. Upon counting all the electrons in the molecule there are two pairs of nonbonding electrons $(1s)^2(1s)^2$, four pairs of bonding electrons $(\sigma 2s)^2$, $(\pi 2p)^4$, $(\sigma 2p)^2$, and one pair of antibonding electrons $(\sigma^* 2s)^2$. The resultant effect is that of three bonding pairs, which correspond to a triple bond between the two nitrogen atoms.

4-16 Polar Molecules. The distinction between covalency and electrovalency is not sharp. Probably the only pure covalencies are bonds which unite two identical atoms. In most cases bonding can best be described as either covalency with some electrovalent character or electrovalency with some covalent nature.

The combining of atoms to form molecules may bring into existence an unequal distribution of electron densities between the atoms making up the molecule. This distribution may range from an exchange of electrons to a completely equal sharing of electron densities between atoms within a molecule. For example, in the formation of a molecule of sodium chloride in the vapor state, the sodium and chlorine atoms have opposite charges and are separated by a characteristic internuclear distance. Such a molecule may be designated as ionic since an electron has been sufficiently removed from one atom to impart opposite charges on the two atoms within the molecule. On the other hand, in the formation of the chlorine molecule Cl_2 , the single $3p$ electron of each chlorine atom is coupled to form an electron pair. This electron pair is shared mutually

by each atom and serves to fill the incomplete $3p$ orbital in each chlorine atom. The electronic structures of these compounds are represented diagrammatically in Fig. 4-13. Intermediate between these two extreme types of compounds there is an important group of molecules in which the electrons are incompletely transferred and unequally shared. For instance, when two atoms combine to form a simple molecule, unless the atoms are identical, the electron pair which makes up the bond will be drawn more closely to one atom than the other. Or, in terms of the quantum theory, the electron clouds making up the bond are more dense in the region of one atom than in the other. In a molecule containing two dissimilar atoms there is a displacement of electric charge so that the

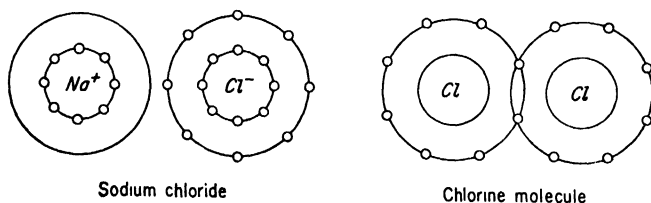


Fig. 4-13 Diagrammatic representation of the electronic structure of sodium chloride and the chlorine molecule.

center of positive charge does not coincide with the center of negative charge. The bond so produced is partly covalent and partly electrostatic. Molecules containing displaced electron pairs are described as *polar*, and the forces which hold them together may be called *polar bonds*. Examples of such molecules are H_2O , HCl , and NH_3 .

An atom may be regarded as a positive center with an atmosphere of negative charges about it. In the case of the chlorine molecule two atoms of the same radii and with positive nuclear charges equal to each other have combined to fill incomplete orbitals. In the resulting molecule the electron densities of the chlorine atoms are the same, and therefore the bond is completely covalent in character. When two atoms of different radii, with positive centers of different magnitudes, combine to share an electron pair, the most probable position of the latter will not be equidistant from the two positive centers. An excellent illustration of the electronic structure of such a molecule is furnished by iodine monochloride, ICl . The chlorine atom is smaller than the iodine atom, and in the ICl molecule the attractive force of the positively charged nucleus of the chlorine atom for the electron pair is greater than that of the iodine atom. For this reason the two electrons making up the bond are drawn nearer to the chlorine atom than to the iodine atom, giving the chlorine atom a slightly negative charge and the iodine atom a slightly positive charge, as indicated in Fig. 4-14. Such a molecule never actually ionizes

into negative chloride ions and positive iodine ions, but the molecule is electrically unsymmetrical. This accounts for the fact that polar molecules exhibit certain physical and chemical properties that are characteristic of ionic compounds. For example, polar solvents such as water and ammonia will dissolve ionic compounds more readily than covalent compounds. The electrical dissymmetry in polar molecules which results in separate positive and negative centers accounts for their magnetlike properties in an electrostatic field.

A molecule containing separate negative and positive charges is known as a *polar molecule*, and the degree of polarity depends upon the distance between charges within the molecule. Ordinarily the degree of polarity

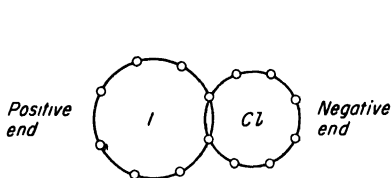


Fig. 4-14 A diagrammatic representation of the electronic structure of the iodine monochloride molecule.

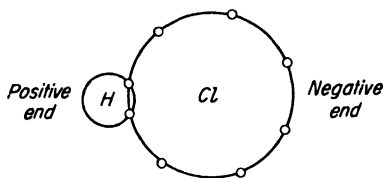


Fig. 4-15 A diagrammatic representation of the electronic structure of the hydrogen chloride molecule.

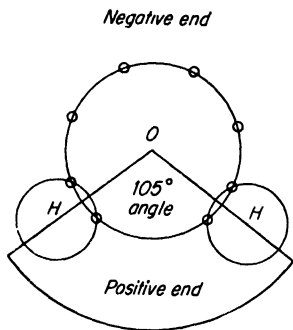
is designated as the *dipole moment* of the molecule, and the dipole moment is calculated by multiplying the charge on one of the atoms by the distance between the centers of the two charges. The magnitude of a dipole moment cannot be predicted quantitatively with any degree of exactness, but it can be determined by a number of experimental methods. In the case of diatomic molecules the attractive forces exerted by the two positive nuclei for the electron pair are related to the magnitude of the nuclear charges and the radii of the two atoms. The hydrogen chloride molecule illustrates the combination of two atoms with widely different radii and nuclear charges. Despite the smaller size of the hydrogen atom the greater nuclear charge of the chlorine atom causes the electron pair to be shifted toward the chlorine atom. Consequently the separation of charges in the HCl molecule, as shown in Fig. 4-15, is such that the chlorine atom is negatively charged with respect to the hydrogen atom.

In the case of polyatomic molecules an explanation of polarity becomes more complex. It is quite certain that the shape of a polyatomic molecule may affect the extent to which there is an effective separation of charges within the molecule. Thus the water molecule, which has an angular structure in which the two hydrogen atoms are on the same side of the oxygen atom, has a permanent dipole moment. This results from the fact that the two singly occupied $2p$ orbitals in the oxygen atom form directed bonds (Sec. 4-13), which are theoretically at right angles to each

other. When the oxygen atom combines with two hydrogen atoms to form a molecule of water, the OH bonds establish an angle of 105° with each other. This distortion¹ from a right angle is believed to be due to forces of repulsion operating between the two hydrogen atoms. As indicated in Fig. 4-16, the oxygen side of the molecule is negatively charged, and the hydrogen side is positively charged.

The dipole moment of a molecule may be treated as a vector. For example, the carbon dioxide molecule is found experimentally to have a zero dipole moment, although it is certain that each of the CO bonds has a permanent dipole moment. This is to be expected because of the differences in nuclear charges and atomic radii of the carbon and oxygen atoms. However, the fact that the CO_2 molecule exhibits a zero dipole moment indicates that the two bond moments must neutralize each other within the molecule. Such a cancellation of bond moments is possible only if the molecule is linear with the carbon atom at the center. The carbon tetrachloride molecule CCl_4 is another molecular structure that should be expected to have internal polarity. Chlorine has a greater electron affinity than has carbon, and the shared electrons should be so distributed in each carbon-chlorine bond as to produce a permanent dipole, with the chlorine atom acquiring a slightly negative charge and the carbon atom a positive charge. The fact that the molecule, as a whole, has a zero moment can be explained only by assuming a symmetrical arrangement in space for the four bonds, so that the dipole of one balances the dipole of another.

Fig. 4-16 A diagrammatic representation of the electronic structure of the water molecule, showing the angle formed by the two OH bonds.



4-17-² **Electronegativity and Bond Type.** In a diatomic molecule the magnitude of the dipole moment, or, to use a more general term, the *polarity* of the covalent bond, depends primarily on the difference in the electronegativity of the two elements forming it. The term *electronegativity* refers to a number of properties which may characterize an element, none of which can be defined with exactness. Pauling describes electronegativity as the power of an atom in a molecule to attract electrons to itself. Furthermore he states that this property differs from the electrode potential, ionization potential, and electron affinity, although it is related to these properties in a general way. Actually, for a univalent atom, the average of the ionization energy and the electron affinity is a

¹ Another explanation for this distortion is given in the footnote in Sec. 4-13.

measure of its electronegativity, but this generalization does not extend to multivalent elements.

From heats of formation of the most common elements in some of their compounds Pauling has set up an arbitrary electronegativity scale for atoms of these elements. Table 4-12 lists the relative electronegativities of some of the more common elements. From the relative positions of the elements on this scale a prediction can be made as to the type of bond which may be formed between two atoms. According to Pauling, if the

TABLE 4-12 RELATIVE ELECTRONEGATIVITY OF THE ELEMENTS

<i>Element</i>	<i>Relative electro- negativity</i>	<i>Element</i>	<i>Relative electro- negativity</i>
Cesium	0.7	Antimony	1.8
Rubidium	0.8	Silicon	1.8
Potassium	0.8	Boron	2.0
Sodium	0.9	Arsenic	2.0
Barium	0.9	Hydrogen	2.1
Strontium	1.0	Tellurium	2.1
Lithium	1.0	Phosphorus	2.1
Calcium	1.0	Selenium	2.4
Magnesium	1.2	Iodine	2.4
Yttrium	1.3	Carbon	2.5
Scandium	1.3	Sulfur	2.5
Beryllium	1.5	Bromine	2.8
Aluminum	1.5	Chlorine	3.0
Zirconium	1.6	Nitrogen	3.0
Titanium	1.6	Oxygen	3.5
Tin	1.7	Fluorine	4.0
Germanium	1.7		

separation on the scale is 1.9, the bond is 50 per cent ionic in character. When the separation is greater than 1.9, the bond is correspondingly more ionic; however, this rule is not rigid in its application. The approximate relation between the amount of ionic character of a single bond between two atoms A and B , and their electronegativity difference $x_A - x_B$ is given in Table 4-13.

Certain conclusions may be drawn from the relative negativities and electronegativity differences as given in Tables 4-12 and 4-13. These values indicate that the bonds between alkali metals and nonmetals are more than 50 per cent ionic. Magnesium and the alkaline earth metals form essentially ionic bonds with the more electronegative elements. The bonds formed by Al, Be, B, and Si vary widely in their ionic character, ranging from less than 1 per cent for the B—H bond to more than 70 per cent for the Al—F bond. The most ionic carbon bond is C—F, with 43 per cent ionic character, and the bonds from fluorine and oxygen to all metals are essentially ionic. In nonmetallic oxides and fluorides

202 Fundamental Concepts of Inorganic Chemistry

the bonds have an appreciable ionic character, but most molecules composed of other nonmetals are essentially covalent.

Since the electronegativity scale is derived from the heats of formation for certain univalent elements, it would seem that electronegativity values could also be used to determine heats of formation. However, the agreement between the predicted and observed heat of formation is only approximate. There are apparently factors other than electronegativity affecting the heats of formation of substances; therefore the electronegativity scale becomes a more or less empirical method for assessing bond type. As such, numerical values for percentage ionic character of bonds

TABLE 4-13 PARTIAL IONIC CHARACTER OF BONDS AND ELECTRONEGATIVITY DIFFERENCE OF ATOMS*

$x_A - x_B$	Partial ionic character, %	$x_A - x_B$	Partial ionic character, %
0.0	0	1.4	32
0.2	1	1.6	40
0.4	3	1.8	47
0.6	7	2.0	54
0.8	12	2.2	61
1.0	18	2.4	68
1.2	25	2.6	74

* Linus Pauling, "General Chemistry," p. 235, W. H. Freeman & Co., San Francisco, 1953.

are roughly qualitative, never quantitative. Moreover the application of this method to multiple bonds is more difficult and, so far, less successful.

4-18 ✓ Some Physical Properties of Covalent Compounds. Molecules in which all the bonds are essentially covalent are comparatively few in number. However, when we speak of covalent compounds, we ordinarily include all molecules which do not ionize. Substances made up of such molecules usually occur as gases or liquids under ordinary conditions. Only if their molecular weight is high are they solids. The relation of physical state to magnitude of molecular weight is well illustrated in the common halogens. Chlorine with a molecular weight of 71 is a gas, bromine with a molecular weight of 160 is a liquid, and iodine with a molecular weight of 254 is a solid. Other common nonionizing molecules which are gases include hydrogen chloride, ammonia, and methane. It is not surprising that carbon tetrachloride with a fairly high molecular weight is a liquid and that paraffin with an even higher molecular weight is a solid.

Molecules whose atoms are bonded covalently have a small external field of force; consequently the work necessary to separate the molecules in a solid or liquid is small. Therefore, as a general rule, covalent com-

pounds have low boiling points. The differences between the boiling points of several ionic and covalent compounds are indicated in Table 4-9. For example, SiCl_4 boils at 58°C and NaCl at 1440°C . The wide difference between the boiling points of the two types of compounds may be explained as a difference in strength between coulombic and intermolecular binding forces. The former is invariably strong, whereas the latter is usually weak.

The weak forces which hold molecules together may be described in terms of dipole, hydrogen, and van der Waals bonding. These forces are discussed more completely in Secs. 4-24 to 4-26. For the present it is sufficient to treat the three types of molecular bonding collectively and state that molecular compounds tend to form soft crystals, indicating that the forces which come into play are relatively small as compared with those in ionic crystals. These soft crystals have relatively low melting points and usually sublime readily. Iodine is an excellent example since it not only has a low melting point but also sublimates easily.

Most covalent substances exist as molecules, which are held together rather loosely, and such substances generally possess low melting and boiling points. In addition to these substances which occur as soft crystals, liquids, or gases, there is another group of covalently bonded substances in which the molecules have lost their identities. These latter substances normally occur as solids and are usually designated as atomic (homopolar) crystals. Any one of these crystals must be considered as one gigantic molecule. Typical examples are Si, SiC , AlN , and C in the form of diamond. They are insulators in both the solid and the molten state and usually possess diamondlike hardness. Their melting points are high, as are their refractive indices. As a general rule, atomic crystals are formed by the lighter elements of the middle columns of the Mendeleev periodic table.

THE METALLIC BOND

Approximately three-fourths of the one hundred elementary substances are metals. The use of certain metals, such as gold, silver, copper, tin, and lead, dates back to the time of the ancient Egyptians and Babylonians. Our present mechanical civilization is made possible by the properties which characterize metals and their alloys. A metal may be defined as a substance which is a good conductor of electricity and heat, and which possesses a bright appearance called *metallic luster*. Also, certain mechanical properties such as high tensile strength, malleability, and ductility are usually associated with the metallic state. However, in spite of the long-continued usage of some of the more common metals and the extensive physical and chemical investigations expended on them, the nature of

the bonding between the atoms in a metal has been until recently a matter of very unsatisfactory speculation.

Two different theories of metallic structure have been advanced to account for the various physical properties which distinguish metals as a class. The quantum-mechanical theory of metals has been developed by Sommerfeld, Bloch, and others. This theory can be compared with the molecular orbital approach to molecular structure, inasmuch as the electrons in a metallic crystal are regarded as belonging to the crystal as a whole rather than to individual atoms. An alternate approach to the

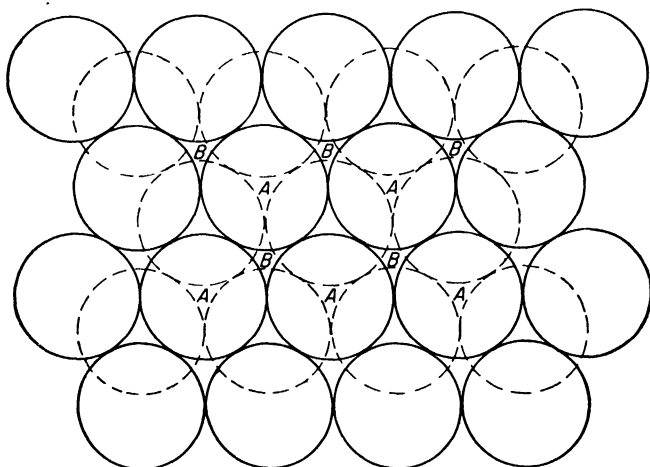


Fig. 4-17 Close-packed atoms in metal crystals.

theory of metallic bonding has been offered by Pauling which involves resonance between a number of structures with one-electron and electron-pair bonds. According to Pauling the metallic bond has essentially a covalent character, and his approach might be compared to the Heitler-London concept of electron-pair bonds in molecular structures.

4-19 The Metallic State. Metals possess a unique structural arrangement of atoms which differs widely from that in nonmetals. Most metals crystallize with an atomic arrangement in which the atoms acquire as many neighboring atoms as is geometrically possible. X-ray examination of metals reveals that the closest packing arrangement of atoms may produce three forms of crystals. The great majority of metallic elements crystallize as either a face-centered cubic lattice or a close-packed hexagonal lattice, although a few acquire a body-centered structure.

The term *close packing* describes that arrangement in which a given number of equal spheres occupy the minimum amount of space. Atoms are spaced in crystals in precisely the same way that spheres would be

spaced to form a closely packed arrangement. This is not to imply that atoms possess the relative rigidity or density of large spherical solids; however, since the packing is the same for both types of bodies, we shall treat atoms as if they were rigid spheres. In the closest-packed arrangement a number of spheres in one plane are so arranged that each sphere is in contact with six other spheres in the same layer. This arrangement is illustrated by the heavy circles in Fig. 4-17. A second layer is formed by placing spheres in the depressions formed where the spheres meet in the lower layer, as indicated by the dotted circles. Again each sphere

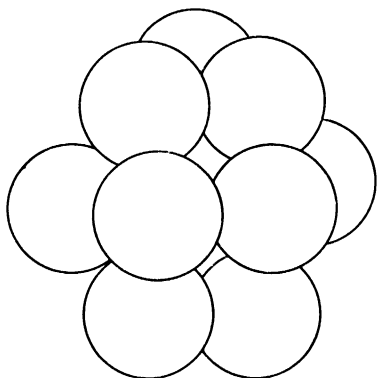


Fig. 4-18 A diagrammatic representation of hexagonal close packing of atoms within metal crystals.

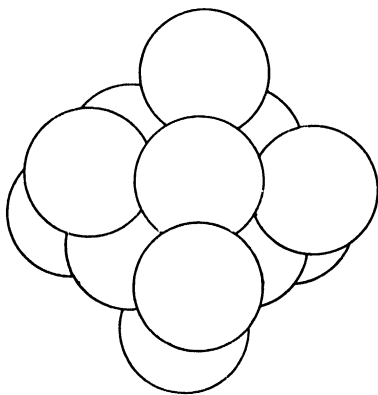


Fig. 4-19 A diagrammatic representation of the face-centered cubic type of packing in atoms.

touches six others in the same layer. A third layer of the same type may be built up in two alternate ways, since there is now a choice of two kinds of depressions. Either the spheres may be placed in the depressions marked *A*, in which case the spheres will be vertically above the spheres in the first layer, or they may be placed in the depressions designated as *B*, thereby giving a different type of close packing. In the latter arrangement the spheres in the fourth layer will correspond with those in the first. When the spheres are placed in the depressions marked *A*, the resulting structure is called *hexagonal close packing* since the entire structure can be considered as being made up of hexagonal units such as the one shown in Fig. 4-18. If the spheres are placed in the depressions designated as *B*, the structure so produced is called *face-centered cubic close packing* because the whole structure can be thought of as being made up of cubical units (see Fig. 4-6, in which there is a sphere at each corner of the cube and a sphere in the center of each face). Figure 4-19 illustrates the face-centered cubic type of packing in atoms.

In both hexagonal and cubic close packing each atom or sphere has

12 nearest neighbors. Therefore those metals containing either of these atomic arrangements are said to have a coordination number of 12. About 50 of the 70-odd metals crystallize into one, or both, of these close-packed lattices. Typical examples of metals with face-centered cubic lattices are Pb, Ag, Au, Al, Cu, Co, and Ni. Among those with a hexagonal structure are Mg, Cd, Os, Zr, and Zn.

Another common structure, adopted by about 20 metals, is the *body-centered* cubic structure. This method of packing, which is illustrated in Fig. 4-20, is less economical in space than the other two types of metal lattices. The structural unit in this case is a body-centered cube, in which there occurs an atom at each of the eight corners of a cube and another in the center. Each atom, therefore, has eight nearest neighbors, and metals which crystallize into the body-centered cubic pattern have a coordination number of 8. Figure 4-6 illustrates a body-centered cubic unit. Typical elements with this form of packing are Ta, Nb, Mo, V, and all the alkali metals.

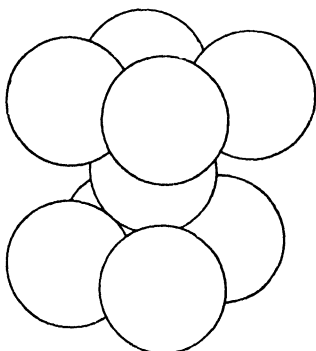


Fig. 4-20 A diagrammatic representation of the atoms associated with a unit cube of the body-centered cubic type of packing in metals.

4.20 The Bloch-Sommerfeld Theory of Metals. The close-packing structure which prevails in metals results in a high coordination number, usually 8 or 12.

These high coordination numbers and the fact that atoms of metals are relatively poor in valence electrons rule out any possibility of the existence of ordinary covalent bonds as linkages between metallic atoms. There are not enough valence electrons to form electron pairs between each metallic atom and all its neighbors. Furthermore the physical properties of metals are so unlike those of ionic compounds that the presence of electrostatic forces operating between atoms within a metal is highly unlikely. Nevertheless metallic crystals possess considerable strength, which indicates the presence of forces greater than those of the van der Waals type (Sec. 4-26). It becomes necessary, therefore, to postulate the presence of a special type of bond, designated as the *metallic bond*, by which a large number of valence-poor atoms may be bound together.

In order to account for the special properties exhibited by metals, such as high thermal and electric conductivities, one of the earlier theories proposed that metal atoms are packed in the form of ions in a close-packed structure and that the electrons acting as a gas are diffused throughout the crystal lattice. Later Pauli suggested that the free electrons are

restricted to a set of continuous or partially continuous energy levels in such a manner that they are identified not with particular atoms but rather with the crystal as a whole. Although this theory accounted for many of the special properties of metals, it raised about as many questions as it answered. One particular problem was to explain the specific heat of the electron gas. According to the kinetic theory the specific heat of an ideal gas is 3 cal/mole at constant volume. Consequently, if metals contain an electron gas, the specific heat of a metal should be substantially larger than the specific heat of an insulator. However, no such difference is to be found between these different substances, indicating a serious contradiction in the electron-gas concept.

A solution to this dilemma was proposed by Sommerfeld in 1928. Applying quantum mechanics to the hypothetical electron gas, he showed that this gas has not the distribution of velocities demanded by classical statistics but instead those which correspond with the Fermi-Dirac type of statistics. It is beyond the scope of this presentation to attempt an adequate explanation of the difference between these types of statistics. However, from a qualitative standpoint, the hypothetical electron gas can be described as being a degenerate gas. The electrons constituting this gas are in a degenerate condition in which all low-lying quantum states are tightly occupied. If the degenerate gas is heated the majority of the electrons are incapable of accepting energy since all the neighboring states are occupied. Only a few electrons in the highest quantum states are able to transfer heat into kinetic energy. Thus the electrons make only a slight contribution to the specific heat of a metal, because only a very small fraction of the electrons are capable of thermal excitation.

An additional clarification of the metallic bond has been worked out by Bloch and others. According to their concept the nucleus of each atom in a metallic crystal is surrounded by a series of concentric zones, each zone representing some definite potential. Such a configuration arises because of the wave character of the electron, which restricts the electron energies to certain "permitted" bands. The permitted bands are called *Brillouin zones*, between which are empty bands of "forbidden" energies, and to cross these empty bands requires a large amount of energy. In this concept the energy band, or Brillouin zone, corresponds to one quantum level in an isolated atom, and the bands of forbidden energies are similar to the jumps in energy from one quantum state to the next. The outermost zones contain only those electrons which have acquired sufficient energy from vibrating nuclei to be lifted to these levels. The breadth of a zone depends on the overlapping of the electron clouds. This is large for the outermost electrons, which are contained in a large number of energy levels closely spaced in the permitted band. For the

inner electrons of the constituent atoms the breadth of the band is extremely small. Therefore the inner electrons have essentially the same energy that they would possess in the isolated atoms; moreover they do not participate in interatomic bonding. Because of the close packing in metal atoms the outermost zones of highest potential (around neighboring nuclei) may overlap to some extent. The high-energy electrons which exist in the overlapping zones are no longer identified with particular atoms but belong to the crystal as a whole and may be considered as being mobile. It is these mobile electrons which produce the metallic bond. The Pauli exclusion principle applies to electrons in the overlapping zones, which may be designated as "molecular" energy levels. Therefore, as in atoms, no more than two electrons can enter the same molecular orbital, and then only if they have opposite spins.

4.21 The Pauling Theory of Metals. Pauling's approach to the problem of binding in metals is essentially a modified version of the valence-bond method that was used in explaining covalency (Sec. 4-11). According to Pauling the structure of metals and alloys may be described in terms of covalent bonds that resonate among the alternate interatomic positions in the metals. Although the number of nearest neighbors of an atom in a metal exceeds its valence electrons, Pauling postulates that resonance permits the existence of normal covalencies which resonate between all the possible equivalent pairs of atoms. For example, the metal potassium, whose atoms possess one valence electron, crystallizes into a body-centered structure so that each atom has eight equivalent neighbors, together with six other close neighbors. Since each potassium atom has only one valence electron, an electron-pair bond can be formed with only one neighbor at one particular time; however, the concept of resonance permits the bonding electron pair to be considered as existing at first between one pair of atoms, and then another, and another, etc. Consequently, the distribution of valence bonds, each containing an electron pair, may be represented for a crystal of potassium metal in the following structures:



These structures indicate the possibilities of two bonds to one atom and none to another, which implies that the metallic bond possesses characteristics of both ionic and covalent bonding; however, because of the resonance variations it must be different from either. Furthermore, to account for the properties of a metal, the valence bonds must be considered as resonating at random among the various possible positions.

Pauling regards the potassium atom as well as about three-fourths of

all other metal atoms as possessing an extra orbital in addition to those normally occupied by unshared or bonding electrons. This particular orbital is called the *metallic orbital*, and it plays a special role in metallic resonance. In the resonating structures for the potassium metal one of the atoms has formed two bonds by attaining the K^- configuration. To form the extra bond, this particular atom must be holding two electrons instead of one, as in the normal atom. Therefore the atom designated as K^- must have an extra orbital available, and this is the so-called metallic orbital.

Pauling's theory is of proved value in its correlation of the metallic properties of the elements with the valence theory. It is also more satisfactory than the molecular-orbital theory in explaining such properties as lattice energies, bond distances, and magnetic behavior.

4.22. Alloys. When two or more metals are melted together and the resulting liquid is allowed to solidify, the product is called an *alloy*. The properties of alloys are usually quite different from those of the metals of which they are composed, and the wide range of special properties which may be produced in alloys makes this class of substances of great industrial value. When mixtures of metals in a liquid state solidify, crystals of several forms may result. These various types of alloys may be classified loosely as: (1) those in which a mixture of the components have crystallized separately; (2) those in which a solid solution is formed; and (3) those in which the components have combined to produce intermetallic compounds. It should also be stated that many commercial alloys contain more than one type of structure, depending upon the special properties which may be desired.

Alloys Whose Components Crystallize Separately. The zinc-cadmium alloys serve to illustrate a binary system in which the components crystallize from the melt without the formation of solid solutions or intermetallic compounds. An alloy of this kind is composed of an intimate mixture of small crystals of the component metals in a relatively pure state. It frequently happens that these mixtures have freezing points which are lower than the separate freezing points of any of the components. A concentration-temperature diagram for the Zn-Cd system is shown in Fig. 4.21. Temperatures are indicated on the vertical axis, and the percentages of cadmium and zinc are shown on the horizontal axis. The freezing-point curve reaches a minimum at 264°C when the alloy mixture contains 17.9 per cent of zinc and 82.1 per cent of cadmium. The melting point of zinc is 419.4°C , and that of cadmium is 320.9°C ; therefore this minimum point is lower than the melting points of either of the components or of any other mixture of them. A mixture of this particular composition is called a *eutectic mixture*, and the minimum point on the cooling curve is called the *eutectic point*. Any further analysis of this cooling curve is of

no interest as far as crystal structure or metal binding is concerned. Nevertheless it should be emphasized that the melting point of an alloy of this type, consisting of a mixture of individual metal crystals, depends directly upon its percentage composition.

: *Alloys in Which a Solid Solution Is Formed.* When a molten solution containing two metals which are miscible in all proportions, both in the liquid and in the solid state, is permitted to solidify, the crystals that separate contain both components in continuously varying proportions.

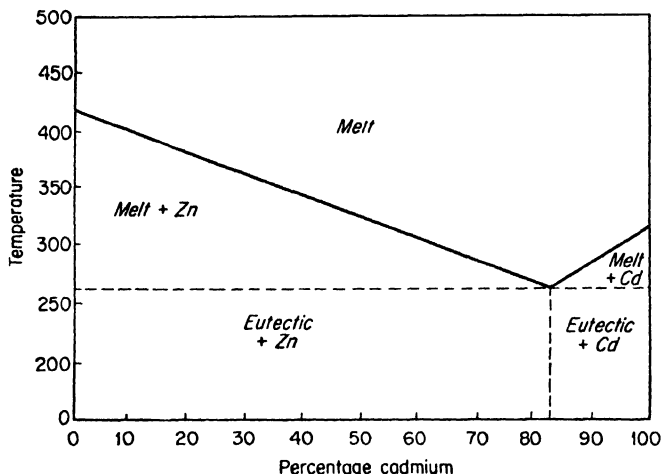


Fig. 4·21 Concentration-temperature diagram for zinc-cadmium alloys.

In other words, there is a complete range of solid solutions having any composition from 100 per cent of one component to 100 per cent of the other component. X-ray analysis of solid solutions show that atoms of one metal replace those of the other at random in the space lattice (Fig. 4·22), provided that the two metals have the same lattice structures and that their atoms do not differ greatly in size. To be more specific, when the atomic radii differ by not more than 10 per cent, the two metals will usually dissolve to form solid solutions, and if they have the same number of valence electrons, they will almost always be miscible in all proportions. If one atom is larger than the other, its entrance into a metal lattice will produce a strain and only a limited number of the larger atoms may be accommodated within the crystal.

Two types of solid solutions are recognized: (1) *substitutional* solid solutions and (2) *interstitial* solid solutions. Alloys of the first type contain two metals whose atoms have radii that are identical, or nearly so. The structures of these solids indicate that atoms of either element may be

substituted, at random, for atoms of the other metal. For example, nickel atoms with radii of 1.243 Å may be substituted for copper atoms with radii of 1.275 Å in the cubic closest-packed copper crystal in any proportions. Since the nickel atom is slightly smaller than the copper atom, there may be a slight change in lattice dimensions, but not in the method of packing. The random replacement of one element by another is indicated diagrammatically in Fig. 4-22. Interstitial solid solutions are those alloys in which very small atoms of nonmetallic elements, such as carbon, boron, and nitrogen, occupy positions in the interstices (open

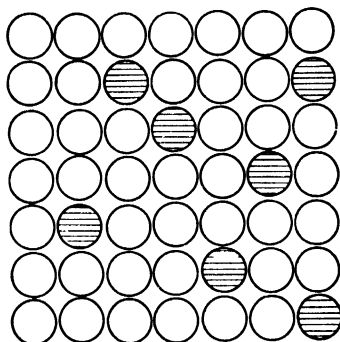


Fig. 4-22 Substitutional solid solution showing random replacement of atoms of one element by atoms of another.

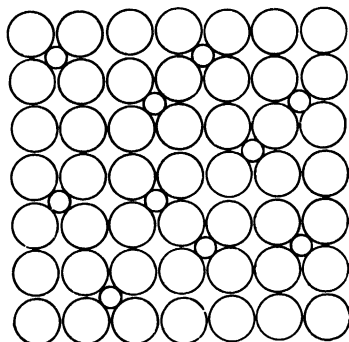


Fig. 4-23 Interstitial solid solution showing random penetration of small atoms into the empty spaces within a lattice of metal atoms.

spaces between atoms) of the metal lattices. A lattice arrangement of this type is indicated in Fig. 4-23.

In closely packed crystals there are holes of two kinds, which may be designated as *tetrahedral holes* and *octahedral holes* because the atoms occupying these holes have four and six neighbors, respectively. There is an upper limit to the size of atoms which may be inserted into the spaces between closely packed metal atoms. If the radius of the atoms in the lattice is taken as unity, the maximum radii of inserted atoms are 0.41 for a tetrahedral hole and 0.59 for an octahedral hole. It is not necessary for all holes of a given type to be occupied since the lattice is stable without the interstitial atoms; however, the presence of interstitial atoms does change the properties of the original metal. The properties so produced indicate that the small atoms of the interstitial elements may establish covalent bonds with neighboring metallic atoms. Consequently the number of mobile electrons within the lattice is reduced, and electric conductivity is greatly reduced in comparison with the conductivity of the pure metal. Furthermore the strong bonds formed by covalent union produce a strong and rigid structure. Therefore it is not surprising that

212 Fundamental Concepts of Inorganic Chemistry

the majority of interstitial combinations have extremely high melting points and that many of them are nearly as hard as diamond. Alloys of this type are usually restricted to those metals in or near the transition region of the periodic table, and the interstitial elements are invariably either carbon, nitrogen, or boron.

Alloys in Which the Components Have Combined to Produce Intermetallic Compounds. When two metals do form a continuous range of solid solutions, one or more intermediate phases may be formed. These phases, differing in crystal structure from the component metals, are frequently referred to as *intermetallic compounds*, although they are unlike true

TABLE 4-14 RATIO OF FREE ELECTRONS TO ATOMS IN ALLOYS

Structure with electron:atom ratio of 3:2	Structure with electron:atom ratio of 21:13	Structure with electron:atom ratio of 7:4
CuZn	Cu ₅ Zn ₈	Cu ₃ Sn
AgCd	Cu ₉ Al ₄	CuZn ₃
AuZn	Fe ₅ Zn ₂₁	AgZn ₃
CuBe	Cu ₃₁ Sn ₈	Ag ₅ Al ₃
CoAl	Ni ₅ Zn ₂₁	Au ₃ Sn
Cu ₃ Al	Na ₃₁ Pb ₈	AgCd ₂
Cu ₅ Sn	Ag ₅ Cd ₈	CuBe ₃

chemical compounds in being somewhat variable in composition. It is true, however, that the two metals usually appear in stoichiometric proportions, but these proportions follow no ordinary valence rules.

Certain relations between the capacity for forming compounds and the positions of the metals in the periodic table have been observed. A metal rarely combines with another of the same group, and never with another of the same subgroup. Also, a metal combines with all the members of a subgroup, or with none of them; however, there are exceptions to this latter rule.

An excellent illustration of the formation of intermediate phases is furnished by the ~~three~~ different types of brass, which are intermediate in composition between the solid solution of zinc in copper and a solid solution of copper in zinc. Between certain percentage ratios of copper and zinc, three different forms of brass, called β , γ , and ϵ phases, may exist. The β form is body-centered cubic, the γ form has a complex cubic structure containing 52 atoms in the unit cell, and the ϵ form has a closely packed hexagonal lattice with dimensions which differ appreciably from those of zinc. Alloys of metal pairs other than copper and zinc may form β , γ , and ϵ phases with the same crystal structures as the different brasses, provided they have the same electron:atom ratio. To explain the refer-

ence to *electron:atom ratio*, it has been observed that, if the number of valence electrons in an intermetallic compound is divided by the number of atoms in the compound, a definite ratio is obtained for each type of phase. These ratios are commonly called the *Hume-Rothery ratios*. The ratio for the β phase is 3:2 (or 21:14); for the γ phase it is 21:13; and for the ϵ phase the ratio is 7:4 (or 21:12). A selection of phases with the β , γ , and ϵ structures is given in Table 4-14.

The properties of intermetallic compounds vary with their structure. As a general rule, the β type is strong and ductile, whereas the γ and ϵ types are so brittle and hard as to render them almost useless. The latter two types are also poor conductors of heat and electricity. Because of this high resistance to conduction it appears that the bonds between atoms in these two phases cannot be true metallic bonds but must be, to some extent, homopolar¹ or covalent.

Certain alloys which are random solid solutions when rapidly cooled from a molten state may undergo rearrangement to produce intermetallic compounds when subjected to special heat-treatments. X-ray analysis shows that copper and gold form solid solutions, but if these solid solutions contain the two metals in the formula-weight ratios of either 1 gfw of copper to 1 gfw of gold or 3 gfw of copper to 1 gfw of gold, it is possible to convert them to the compounds CuAu and Cu_3Au by the process of annealing. When solids of the correct composition are properly annealed, or if a melt of the same composition is allowed to cool very slowly, the copper and gold atoms are found to occupy definite positions in the lattice. When subjected to either of these treatments, it is found that the face-centered lattice so produced contains gold atoms at the corner of each unit cube and the copper atoms at the centers of the faces. Crystals of this kind, in which definite positions in the lattice of a given element are systematically occupied by atoms of another element, are known as *superlattices*, or *superstructures*. The arrangement of atoms in a superstructure is indicated diagrammatically in Fig. 4-24. The process of rearranging atoms in a solid solution to form a superstructure is called *order-disorder transformation*. It should be recognized that if a super-

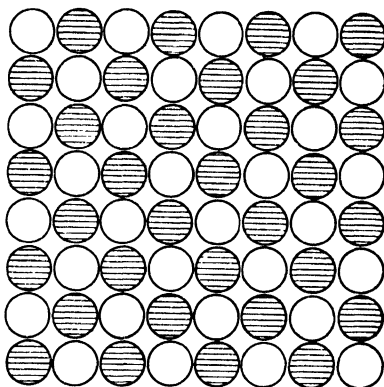


Fig. 4-24 The arrangement of atoms in a superlattice.

¹ A bond in which the electron pair is shared equally by two atoms, as is illustrated by the bonding between the hydrogen atoms in the hydrogen molecule.

structure is possible it must exist at a lower temperature range than the random solid solution. Moreover, if the temperature of a superlattice is raised, the thermal agitation converts the ordered state into a condition of disorder. In other words, the ordered arrangement is a system of lower potential energy than is the disordered distribution.

4-23 Physical Properties of Metals. The theories concerning the "metallic state," or the structure of metals, have largely been developed in an attempt to explain the special properties of metals. Conversely it should be possible to relate the physical properties of the metals to those theories which have been advanced to explain their structure. The particular properties which distinguish metals from other elements may be loosely classified according to three physical characteristics: (1) metals are good conductors of heat and electricity; (2) most metals reflect light totally, a property designated as metallic luster; and (3) nearly all metals are malleable or ductile at ordinary temperatures.

Electric and Thermal Conductivity. A flow of electric current is believed to be a movement of electrons through a conducting material. This implies that a conductor must contain some mobile electrons which may pass freely from one atom to another. We have already noted that metallic atoms are relatively poor in valence electrons; yet in crystal lattices they are in contact with 8 or 12 neighboring atoms. This close-packing structure cannot be attained by either covalent or ionic bonding, and in order to explain metallic bonding it has been suggested that an electron may serve more than 2 atoms. Apparently electric conductivity is possible in a substance only when the total number of electrons is less than the number of possible electronic states. The use of the words "diffuse" or "mobile" cannot accurately describe the electrons which are present in a conductor. "Loosely held electrons" might be a better description. Furthermore, it seems quite certain that the number of electrons which are free to conduct an electric current must be quite small as compared with the number of atoms.

There appears to be a close relation between the conduction of electricity and the conduction of heat. It would seem that the "free" electrons which are the carriers of an electric current must also play an important part in the conduction of heat. This conclusion results from the fact that metals which are good conductors of electricity are also good conductors of heat. However, the mechanism of thermal conductivity is not so well understood as that of electric conductivity, and any attempt to explain the former would involve a high degree of speculation. It is interesting to note that certain theoretical reasoning, which is beyond the scope of this book, predicts that at ordinary temperatures the ratio of thermal and electric conductivities is constant for all metals. This predicted rule, sometimes known as the *Wiedemann-Franz law*, is only

approximately true. Another observation worthy of note is the fact that the univalent metals of Group I in the periodic table, in which the electron deficiency is most marked, possess higher electric and thermal conductivities (per atom) than most of the metals.

Metallic Luster. The color of a substance is due to the effect of electrons vibrating within it. It is assumed that metallic luster results from mobile electrons which have been set in motion by photons of the visible frequencies. In all metals except copper and gold the electrons absorb light of all wavelengths in the visible spectrum. This energy in the form of light quanta is momentarily accepted by mobile electrons and then immediately reemitted in the form of visible light. This momentary exchange of light energy gives rise to the familiar metallic luster.

Malleability and Ductility. The mobile nature of metallic binding between atoms makes possible the deformation of metals without fracture. When a crystal of a metal changes shape, layers of atoms, acting as if they were rigid spheres, slip over each other along definite glide planes, and with little loss of energy. The metals that are the least malleable or ductile are those whose atoms have more than two electrons in the outermost shell. The plasticity of pure aluminum has been used as an argument that it may be a univalent element in the metallic state.

There is good reason to believe that the movement of atoms along a glide plane is in the form of one atom at a time rather than in layers of atoms. Proof of this idea is furnished by the effect of small amounts of impurities on the malleability and ductility of a metal. Thus the presence of a small amount of sulfur in copper makes the latter quite brittle. Apparently foreign atoms produce brittleness by interfering with the flow of metal atoms along the normal glide planes.

OTHER BOND TYPES

We have originally classified the chemical bonds that exist between atoms into three extreme types, namely: electrostatic bonds, covalent bonds, and metallic bonds. In addition to these bond types there are certain other forces which may serve to hold molecules together. It must be admitted that there is not always a clear distinction between the bonds holding atoms together and those operating among molecules. Although the latter forces are usually electrostatic or covalent in nature, they are quite often sufficiently different in their mode of operation to make it worthwhile to consider them as a separate group of bonds.

4.24 Dipole Bonds. In Sec. 4.16 we have attempted to show that there exist certain molecules, called polar molecules, in which the binding between atoms is partly covalent and partly electrostatic in nature. As examples of such molecules, iodine chloride and hydrogen chloride were

cited. Each of these molecules is electrically unsymmetrical inasmuch as the positive center of charge does not coincide with the negative center. Consequently polar molecules will orient themselves in an electric field because of their electrical dissymmetry. Other molecules, such as water, may be polar because the directed valency forces within the molecule produce a separation of positive and negative charge. This separation of charge in a molecule is known as its *dipole moment*, and, quantitatively, the term is defined as *the charge on one of the atoms multiplied by the distance between charges*. Actually the dipole moment arises from a difference in electronegativity (Sec.4-17) between two atoms in a chemical bond, and, therefore, every bond should have a dipole moment connected with it. However, this discussion will be limited to the examination of a few combinations of ions and molecules or molecules and molecules in which the binding forces are not the result of either electron transfer or electron sharing.

Dipole bonds are invariable electrostatic in nature, but the attractive forces between components are weaker than those found in strictly ionic compounds. For example, the force of attraction between an ion and a polar molecule is usually weaker than the force operating between two oppositely charged ions. Nevertheless the forces of attraction in both cases are coulombic in nature and, as such, obey Coulomb's law of electric force. This law states that the magnitude of the electric force between two charged bodies is proportional to the product of the charges and inversely proportional to the square of the distance between them. Among the various possible dipole bonds a few of the more common combinations are produced by:

✓ *Ion-Dipole Bond*. In the previous paragraph it was stated that the electrostatic force existing between an ion and a polar molecule obeys Coulomb's law of electric force. Consequently the strength of this bond depends upon the charge of the ion and the magnitude of the electric dipole. In many cases the bond is quite strong, as, for example, in the union of a water molecule with a proton to form a hydronium ion. The solvation of ions and the dissolution of ionic lattices in polar solvents are believed to result from ion-dipole forces. Also many coordination compounds owe their binding force to this form of electrostatic attraction. A more complete discussion of solvated ions and coordination compounds is given in Chap. 5.

✓ *Dipole-Dipole Bond*. The electric dipole moments of two or more molecules may attract and interact with each other in such a manner as to cause an alignment of opposite poles in the different molecules. This attraction between molecules tends to increase the molecular weight of the substance, since two or more smaller molecules interact to produce, in effect, a larger molecule. A molecular association of this type will

have a higher boiling point than would be normally expected from the simpler molecules. For instance, nitrogen trifluoride, NF_3 , because of directed valencies to the fluorine atoms, has a permanent dipole moment, with the three electronegative fluorine atoms residing on one side of the nitrogen atom. As a result of the permanent dipole moment, molecules of NF_3 may interact by dipole-dipole alignment to produce a larger molecule. Furthermore, on account of this somewhat loose bonding, the boiling point of nitrogen fluoride is at least 60°C higher than might be expected in the absence of dipole bonding.

✧ *Ion-induced Dipole Bond.* Large symmetrical molecules whose centers of positive charge are relatively distant from their electrons may have their electrical symmetry upset when brought in contact with strongly charged ions. The dipole moment produced by contact with a charged particle is said to be an *induced* dipole, and any bonding which may result is an ion-induced dipole bond. A specific example of a combination of this type is the reaction of the iodide ion with the iodine molecule:



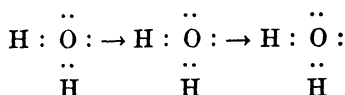
In this reaction the iodide ion has induced a dipole moment in the large iodine molecule, and the source of the bonding is the attraction between the negatively charged ion and the induced electric dipole.

✧ **4.25 The Hydrogen Bond.** The hydrogen atom has the unique ability to form a bond, or bridge, between two other atoms if these two atoms are of elements that are strongly electronegative in character. Since the hydrogen atom has only one stable orbital ($1s^1$) for bond formation, according to the Pauli exclusion principle, it can form only one covalent bond. Yet, despite the fact it can be associated with no more than two electrons, the hydrogen atom without its electron shell may form an additional bond, largely ionic, with an electronegative atom. Thus the hydrogen bond may be thought of as a linkage resulting from the imprisonment of a proton between two electronegative atoms.

Nitrogen, oxygen, and fluorine are increasingly electronegative, in that order, and their linkages with hydrogen are increasingly polar, with the positive charge residing upon the hydrogen atom. It should be noted that chlorine, which is as electronegative as nitrogen, has little tendency to form hydrogen bonds. Presumably this lack of hydrogen bonding is due to the larger size of the chlorine atom, which results in a less intense electrostatic field about the atom. It is extremely doubtful that the hydrogen atom is situated midway between two electronegative atoms, because the hydrogen linkages are of different strengths. In hydrogen bonding between two oxygen atoms, as in water, the covalent bond within the molecule has a strength of 109 kcal/mole, whereas that of the hydrogen bond alone is approximately 5 kcal.

218 Fundamental Concepts of Inorganic Chemistry

The formation of hydrogen bonds is responsible for the association of molecules in water, in which the hydrogen atom forms a bridge between oxygen atoms with unshared electron pairs, such as



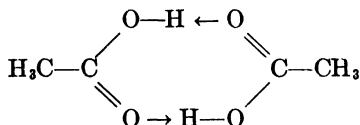
However, this crude diagram is far from representing the true structure of water. Actually the bonds are tetrahedral in their directions and not planar; moreover each electron pair on the oxygen atom may participate in another hydrogen bond. In ice, four molecules of H_2O are coordinated about a central molecule to form a tetrahedral structure. With a rise in temperature some of these bonds are broken; yet sufficient bridges remain between aggregates of two or more molecules to account for the abnormally high boiling point of water. It has been estimated that approximately two-thirds of the heat of vaporization of water at its boiling point is required to disrupt the hydrogen bonds existing at that temperature. The hydrogen bond in HF is even stronger, persisting even in the vapor state. Such bonds account for the fact that gaseous hydrogen fluoride is largely polymerized into the molecular species H_2F_2 , H_3F_3 , H_4F_4 , H_5F_5 , and H_6F_6 . The abnormal boiling points of ammonia, water, and hydrogen fluoride are listed in Table 4-15 with the boiling points of the hydrides of the other members of Groups V to VII of the periodic table. A comparison of these values indicates the remarkable effect of hydrogen bonding upon this physical constant. Normally it might be expected that the boiling points of a series of chemically related substances would increase with molecular weight; consequently, without hydrogen bonding, water should have a boiling point of about -80°C instead of $+100^\circ\text{C}$.

TABLE 4-15 BOILING POINTS, DEGREES CENTIGRADE, OF CERTAIN HYDRIDES

Group V		Group VI		Group VII	
NH_3	-33	H_2O	+100	HF	+19
PH_3	-85	H_2S	- 60	HCl	-85
AsH_3	-55	H_2Se	- 42	HBr	-67
SbH_3	-17	H_2Te	- 2	HI	-35

Not only does hydrogen bonding occur in the simple hydrides of nitrogen, oxygen, and fluorine, it is also responsible for the polymerization of many organic compounds. For example, acetic acid and certain other organic acids may occur as dimers. The hydrogen bonds are so strong in these double molecules that they remain unbroken even in the

gas phase. The structure of the acetic acid dimer is indicated as follows:



§ 4-26 **Van der Waals Forces.** As implied by the name, *van der Waals forces* were originally postulated to explain the deviation of real gases from the ideal gas laws. However, the weak bond produced by these forces is another form of dipole bond and, as such, might be grouped within the classification given in the preceding section. The bonding in this case results from the attraction between induced dipoles on neutral atoms or molecules. Hence the bond could be described as an *induced-dipole-induced-dipole bond*.

Although an atom or molecule may possess a symmetrical electric field, it will still have a dipole moment that continually fluctuates in magnitude and direction. This fluctuating dipole may be attributed to the electronic motion within the neutral atom or molecule. Because of the constant movement of electrons there is a continuous change in the charge intensities within the electronic atmosphere. Thus the electric field of an atom or nonpolar molecule is subject to intensity oscillations causing certain portions of the particle to fluctuate between a state of being positively charged and that of being negatively charged. Moreover the dipole so produced is oriented in one direction as often as in the opposite direction, and the resultant is a zero dipole moment.

When an atom or molecule is brought within a certain range of distance to another atom or molecule, the fluctuating dipole of one particle will influence the fluctuating dipole of the other particle. In other words, the positive portion on one particle, resulting from the change in charge intensity, can increase the negative intensity of a fluctuating dipole on another particle. The positive and negative portions (induced dipoles) on adjacent atoms or molecules attract one another, and thereby produce the so-called van der Waals forces.

Compared with other bonds, van der Waals forces are very weak. If the atoms or molecules in any crystal are united only by these forces, the crystal may be broken down easily. Such a crystal will be quite soft and have a very low melting point. It is only by means of these forces that it is possible to bring about condensation and crystallization (at very low temperatures) in the inert gases. As in other dipole bonds van der Waals forces are electrostatic in character. However, because of the extreme weakness of the bond, the forces of attraction do not follow Coulomb's law of electrostatic force. Instead, for monoatomic

220 Fundamental Concepts of Inorganic Chemistry

molecules, such as the noble gases, the force of attraction is inversely proportional to the seventh power of the distance between the centers of the molecules. Consequently the attraction between the two induced dipoles does not become significant until the molecules are very close together. On the other hand, if the molecules are in contact with each other, a force of repulsion is set up between the outer electron shells of the molecules. Actually the van der Waals forces operate effectively only when the distance between molecules is approximately 5 Å.

The strength of the van der Waals forces is also dependent upon the size and molecular weight of the molecules concerned. In general the attraction between molecules increases with an increase in size and with an increase in molecular weight. This attraction also determines the boiling points of nonpolar molecules, since boiling point is a measure of the energy necessary to disrupt the forces of the van der Waals bond. As might be expected, large, heavy molecules have higher boiling points than have small, light ones. This generalization may be verified by an examination of Table 4-16, in which are listed the boiling points of the inert gases. The table also permits a comparison of the increase in boiling point with an increase in molecular diameter and with an increase in molecular weight.

TABLE 4-16 A COMPARISON OF SIZE, MOLECULAR WEIGHT, AND BOILING POINT FOR THE INERT GASES

Substance	Radius of molecule, Å	Molecular weight	Boiling point, °C
Helium	0.93	2	-269
Neon	1.12	10	-246
Argon	1.54	18	-186
Krypton.....	1.69	36	-152
Xeon.....	1.90	54	-108
Radon.....	2.2	86	-62

As compared with other intermolecular and interatomic forces the van der Waals bond is extremely weak, with a magnitude of the order of 1 kcal/mole. Although van der Waals forces are present in all substances, other binding forces of greater magnitude are also usually present. Consequently the more feeble forces rarely become significant in the discussion of binding forces between atoms.

EXERCISES

1. Explain, with examples, the meaning of the term electrovalence.
2. Describe the operation of the forces which hold a sodium chloride crystal together.

3. What takes place when an ionic crystal is melted?
4. Why is sodium chloride a better conductor of electricity in a molten condition than in the solid state?
5. List the characteristic physical properties of typically ionic compounds.
6. How is it possible for ionic compounds to form large units of matter?
7. Explain why crystals of ionic compounds should be relatively hard and brittle.
8. Explain, with examples, the meaning of the term covalence.
9. Describe the general physical properties of covalent compounds.
10. What elements are most likely to form covalent bonds?
11. Explain the fact that two identical hydrogen atoms can combine to form a hydrogen molecule.
12. What constitutes a polar compound?
13. What is the difference between a polar and a nonpolar compound?
14. Are all covalent compounds nonpolar? Explain.
15. What does the term resonance imply? Illustrate your explanation with examples.
16. Distinguish between an ionic bond and a covalent bond.
17. Why would you expect ionic compounds to have higher melting points than covalent compounds?
18. Why should you expect the melting point of NaCl to be much higher than that of AlCl_3 ?
19. Which compound should be more ionic, AlF_3 or AlCl_3 ? Give reasons for your answer.
20. Stannic chloride is a volatile liquid and a poor conductor of electricity. What type of bonding is to be expected in this compound?
21. Explain the physical properties of sodium chloride, chlorine, and carbon tetrachloride in terms of their structures.
22. Would you expect rubidium compounds to be ionic or covalent?
23. Determine the oxidation number of phosphorus in $\text{Ca}_3(\text{PO}_4)_2$; of nitrogen in HNO_3 .
24. What is meant by the term coordination number?
25. Explain, with examples, the meaning of the term electron affinity.
26. Define the term ionization energy.
27. Why do some elements have more than one ionization potential?
28. Explain what is meant by the lattice energy of a crystal.
29. In terms of lattice structure account for the characteristic physical properties of metals.
30. Describe the differences between the crystal lattices of an ionic compound and a metal.
31. What factors determine the pattern of a crystal lattice?
32. Explain the meaning of the term electronegativity.
33. Compare the electronegativity table with the periodic table.
34. How can the electronegativities of the elements be used to predict what kind of bond will be formed when two elements combine? Illustrate your explanations with specific examples.
35. Would you expect cesium to be more or less electronegative than potassium? Why?

222 Fundamental Concepts of Inorganic Chemistry

36. Explain why bromine is less electronegative than chlorine.
37. Using the electronegativity scale, predict the nature of the bond in each of the following compounds: beryllium fluoride, beryllium bromide, silicon chloride, sulfur fluoride.
38. How is electronegativity related to atomic radius?
39. Explain what is meant by dipole moment. List two molecules that have dipole moments and two whose dipole moments are zero.
40. What forces hold polar molecules together? Explain their source and operation.
41. How is the polarity of a bond related to the electronegativities of the atoms which are held together by the bond?
42. Account for the shape of the water molecule.
43. Explain the occurrence of the hydrogen bond in water and hydrogen fluoride.
44. Why would you expect H_2O to be more polar than H_2S ?
45. Predict which compound is more polar, ammonia or phosphine. Why?
46. Which compound is more polar in character, HI or HF? Why?
47. Indicate how water molecules may be joined by hydrogen bonds.
48. What takes place in the hydrogen valence shell during the process of hydrogen bonding?
49. Discuss the properties of water in relation to the hydrogen bond.
50. Explain the wide difference between the boiling points of methane and water.
51. Write the structure for the dimer of formic acid.
52. What effect does the hydrogen bond have on the physical properties of compounds in which it occurs?
53. State the types of bonds which would be expected in crystals of (a) krypton, (b) ice, (c) carbon tetrachloride, (d) diamond, (e) copper, (f) magnesium nitrate, (g) potassium chloride, (i) hydrogen fluoride.
54. Compare the strengths of the various types of chemical bonds.

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CHAPTER 5

Complex Ions and Coordination Compounds

The above heading is far-reaching in its possible implications. Already we have used a related term, *coordination number*, in connection with crystal configurations and metal lattices. Conceivably our heading might include any phase of structural chemistry, as well as certain aspects of binding forces in chemical compounds. However, our ensuing discussion will not be nearly so ambitious as the title might imply. We shall limit our exposition to a restricted interpretation of the heading. But, even with limited restrictions in meanings, it is impossible to do much more than barely outline and briefly touch upon the many aspects of this broad topic.

INTRODUCTION

The terms *complex ion* and *coordination compound* are frequently used very loosely. Particularly is this true of the first term, which is widely employed as a catchall for many meanings. Yet most of the loose usages cannot be labeled as erroneous because of the large number of connotations that have become attached to the two terms. In a broad sense any ion in which there is more than one atom may be called a complex ion. Also, any symmetrical arrangement of atoms about a central atom, in the construction of a molecule or ion, may be designated a coordination compound. Consequently almost all inorganic substances existing either in solution or in the solid state may be described by one or both of these terms. For the purpose of simplification in the present discussion we shall define these terms in such a manner as to restrict their possible meanings, but, even so, there will occur certain exceptions to our restrictive definitions.

5.1 Definitions of Terms. As was stated in the previous paragraph, any ion which contains more than one atom, as, for example, the sulfate

ion SO_4^{2-} , may be called a complex ion. Therefore a complex ion may be defined as an electrically charged radical or group of atoms, such as $\text{Co}(\text{NH}_3)_6^{3+}$, which has been formed by the direct union of simple ions or by the direct union of a simple ion with neutral molecules.

Despite the foregoing definition, stable ions such as SO_4^{2-} , ClO_3^- , and NO_3^- are usually regarded as simple ions, inasmuch as they are incapable of dissociation into their component parts under ordinary conditions. Therefore we shall limit our definition of complex ions to those ions which are capable of some dissociation into their component parts at ordinary temperatures. In view of this interpretation, complex-ion formation may be considered to be a reaction that is more or less reversible. Also, our concept of what constitutes a complex ion does not include lattice complexes consisting of certain double salts such as $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and alums such as $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, since these substances are complexes only in the solid state. In water solution these compounds usually break down into simpler substances or ions.

The term complex ion carries a broader meaning than that generally assigned to coordination compound. The latter term is usually reserved for those ions or compounds which contain coordinate linkages (Sec. 5-3). A coordination compound is a complex substance in which atoms or groups of atoms have been added beyond the number possible on the basis of electrovalent binding or covalent binding. In such a compound both electrons of the additional linkages are furnished by the linked atom of the coordinated group. More simply, when a metal ion combines with an electron donor, the resulting substance is said to be a coordination compound. For example, the cupric ion combines with four ammonia molecules, in which the nitrogen atom is an electron donor, to produce the ion $\text{Cu}(\text{NH}_3)_4^{2+}$. This definition is not without exceptions. Later we shall encounter coordination compounds which do not contain coordinate linkages. A typical exception is the hydrated aluminum ion, which is clearly a coordination compound, but whose components are held together by ion-dipole linkages.

The bonding between the central cation in a coordination compound and the surrounding particles may be essentially covalent or essentially ionic depending upon the nature of the components involved. An amplification of this statement is contained in Sec. 5-6, but it should be pointed out that the components of a coordination compound may be held together by electrostatic forces as well as covalent linkages. Later we shall learn that the components in the ion FeF_6^{3-} are held together by ionic linkages, whereas the components of the ion $\text{Fe}(\text{CN})_6^{3-}$ are linked with covalent bonds.

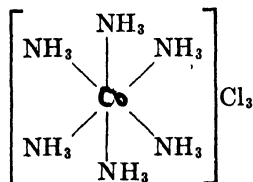
We close this section with the discouraging observation that any attempt specifically to define the terms complex ion and coordination

compound or to differentiate between the two is unsatisfactory because of the many meanings which have become attached to these expressions.

5.2 Werner's Theory of Coordination Compounds. The theory of valence developed during the nineteenth century provided, for that period, a satisfactory explanation of the formation and properties of most organic compounds and the simple salts of the metals. But this early, nonelectronic theory of valence offered no adequate explanation of the union of neutral molecules with ions to form such compounds as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{NH}_3$. To account for the entrance of neutral molecules into chemical reactions, Alfred Werner introduced in 1893 his concept of auxiliary valence. This concept, generally known as Werner's coordination theory was stated as follows:

Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds, called auxiliary valences, may be called into action.

According to Werner the combining power of an atom is divided into two spheres of attraction: the inner, or coordinate, sphere, and the outer, or ionization, sphere. Neutral molecules or oppositely charged ions are coordinated around a central ion in the inner sphere. The number of such groups which may be arranged around the central ion is the coordination number of the ion. He recognized that this arrangement of molecules or ions around the central ion was such as to produce a symmetrical spatial grouping. The coordination numbers which permit spatial symmetry are 2, 3, 4, 6, and 8, of which the values 4 and 6 are most common. On the basis of his auxiliary-valence theory Werner assigned to $\text{CoCl}_2 \cdot 6\text{NH}_3$ the structural formula



The addition of six molecules of ammonia takes place by means of auxiliary valencies. In this complex union the chemical characteristics not only of the ammonia but also of the cobalt ion are lost. On the other hand the chloride ions retain their typical physical and chemical properties. To distinguish between the two spheres of attraction, Werner

introduced the square brackets [] to enclose those atoms making up the coordination complex and which are therefore not ionized.

Not only may neutral molecules be coordinated around a central ion, but ions may also be coordinated in a like manner. Consequently the total electrovalent charge on the complex varies with the number of charged ions which may enter into the coordination sphere to replace neutral molecules. Coordinated molecules may be partially or completely replaced by ions, resulting in a change in the electrovalence of the complex ion. The amines of quadrivalent platinum illustrate these variable combinations. Quadrivalent platinum has a coordination number of 6, and the ammine groups may be replaced by chloride ions to change the valence and nature of the complex in successive steps as indicated in Table 5-1.

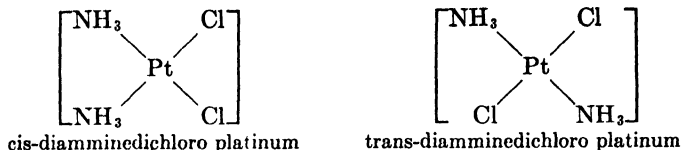
TABLE 5-1 SOME COMPLEX IONS CONTAINING PLATINUM

Formula	Cation	Anion
1 $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_6]^{4+}$	4Cl^-
2 $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	$[\text{Pt}(\text{NH}_3)_5\text{Cl}]^{3+}$	3Cl^-
3 $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$	2Cl^-
4 $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+$	Cl^-
5 $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	Nonelectrolyte	
6 $[\text{Pt}(\text{NH}_3)\text{Cl}_5]\text{K}$	K^+	$[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$
7 $[\text{PtCl}_6]\text{K}_2$	2K^+	$[\text{PtCl}_6]^-$

When an ion replaces a neutral molecule in the inner sphere of a complex, the ion loses its electrovalent character and becomes attached to the central ion by a nonionized linkage. This fact may be verified in the compounds listed in Table 5-1 by precipitating the electrovalent chloride ions with silver ions. In the first complex listed in this table there are four chloride ions which may be precipitated by silver ions. In the second complex only three of the chlorides are precipitated by silver ions, and in the third and fourth complexes only two and one electrovalent chloride ions remain. Complex 5 is a nonelectrolyte, which is almost insoluble in water and consequently, produces no ions in solution. In complexes 6 and 7 the chlorine atoms are bonded by nonionized linkages and cannot be precipitated as simple ions.

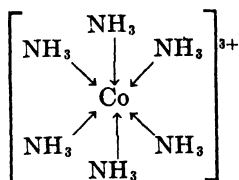
One of the outstanding features of Werner's theory was the assigning of definite positions in space to the groups in a coordination complex. Not only did it provide an explanation of isomerism (Sec. 5-19) that existed among known complex compounds, but it also predicted the existence of isomers of types which had not previously been observed. As an illustration of this phase of his coordination theory Werner showed that the neutral complex of divalent platinum, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, exists in

the form of cis-trans isomers. This type of isomerism is indicated graphically in the following formulas:



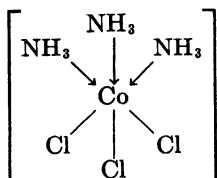
The existence of these isomers also established the proof of the geometric structure of these substances. If the four groups were attached in space at the points of a regular tetrahedron, isomerism would not be possible because the four groups could be interchanged without altering their relation to one another. Consequently, from the fact that isomerism does exist, it may be concluded that the coordinating groups are arranged about the central atom of platinum within one plane (Sec. 5-27).

5-3 Electronic Interpretation of Coordination. Werner's theory was satisfactory at the time it was propounded, when the theory of the electronic structure of matter was unknown. To make the Werner theory compatible with the electronic concept of valence, Sidgwick introduced the idea of a *coordinate bond*, sometimes called the *semipolar bond*. He pointed out the fact that all molecules or ions capable of being coordinated to metals have atoms with at least one unshared electron pair in their structure. According to Sidgwick the auxiliary valence conceived by Werner is a special form of a covalent bond, in which the paired electrons of the bond are furnished by one and only one of the atoms concerned. The atom furnishing the electrons is called the *donor*, and the ion accepting the electrons is called the *acceptor*. Once the bond is formed, it is not different from a covalent bond—the only difference is the mode of formation. For example, the cobaltic ammonia complex is formed by the cobaltic ion accepting 12 electrons from 6 ammonia molecules, and the structure may be represented as follows:



Sidgwick used an arrow to indicate the transfer of an electron pair, and this practice has been followed by many authors. However, this use of an arrow is not entirely justified and in many cases is erroneous in its implications. For example, the nonelectrolyte trichlorotriammino cobalt contains three ammonia molecules represented by arrows as electron

donors and three chlorine atoms which have been converted from electrovalent ions to covalent bonded atoms and represented as covalent linkages. The structural formula for this compound might be written as



This structure appears to indicate a difference in the nature of the bonding of the halogen atom and the ammonia molecule. ✓ Actually there is no difference between the bonds, and they should all be designated as covalent linkages. Hence a coordinate bond may be defined as a covalent bond in which the electron pair was derived from one of the two atoms involved. Furthermore there is no way of distinguishing a coordinate covalent bond from any other covalent bond once the complex is formed. ✓

Sidgwick's electronic interpretation of coordination is not entirely satisfactory. The donation of electron pairs to a central cation would produce an improbable accumulation of negative charge on this ion. In the case of $[\text{Co}(\text{NH}_3)_6]^{3+}$ the donation of electron pairs from the ammonia molecules to the cobaltic ion would result in the cobalt atom becoming negatively charged in respect to the ammonia molecules. ✓ Another difficulty presented by this concept is the fact that the electron pair, available for donation in water, ammonia, and many other neutral molecules, is the $2s^2$ pair. ✓ These electrons have no bonding characteristics (Sec. 4-13), and to excite them to a higher level would require more energy than is usually available in bond formation. ✓ However, the answer to the second objection may lie in the reorganization of energy levels in the bonding atom to form hybrid bonds (Sec. 4-14).

A number of explanations have been offered to overcome the foregoing objections and still retain the Sidgwick donor-acceptor concept of electron-pair bonds. Probably the true explanation of complex formation will evolve on quantum-mechanical lines. In view of the fact that the theory of coordination is still in a state of development it does not seem worthwhile to present the various attempts to preserve the essentials of the Sidgwick theory. ✓

THE NATURE OF THE LINKAGE IN COMPLEX IONS AND COORDINATION COMPOUNDS

The previous discussion may have left the impression that the components of complex ions and compounds are held together only by covalent bonds.

lent or coordinate covalent bonds. This is far from true, inasmuch as many complexes are formed without the donor-acceptor sharing of electrons. Such ions or compounds result from electrostatic forces between their constituents. Therefore it is possible to classify complex compounds rather loosely into those resulting from electrostatic forces and those held together by coordinate covalent bonds.

5.4 Complexes Resulting from Electrostatic Forces between Constituents. A large group of complexes contain ion-dipole bonds. Those hydrated ions which are isoelectronic with the inert gases contain bonds of this type. For example, the ions $\text{Mg}(\text{H}_2\text{O})_6^{++}$ and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ result from the electrostatic attraction between the positively charged cations and the electric-dipole charges within the water molecules. As is explained in Sec. 4-16, the water molecule possesses an angular structure in which the two hydrogen atoms are on the same side of the oxygen atom and the resulting structure produces a permanent dipole moment. This molecule may be visualized as being triangular in shape, with the negative oxygen forming an apex to the triangle, and may be represented diagrammatically as

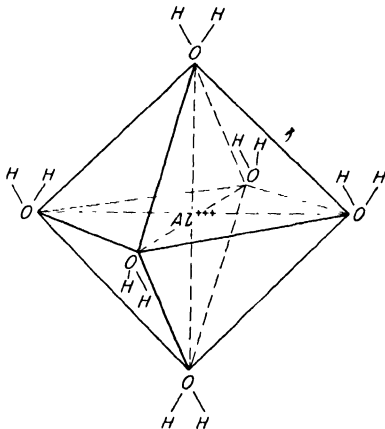
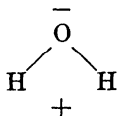


Fig. 5-1 Symbolic representation of the hydrated aluminum ion.



Because of their polar nature, water molecules may be oriented and attracted by ions in water solution. Positive ions are usually smaller than negative ions; therefore cations attract and bind water molecules more tightly to themselves than do anions. The number of water molecules attached to a cation is called its coordination number, and this number is determined by the size of the cation. The hydrated aluminum ion is indicated symbolically in Fig. 5-1.

It would be an oversimplification to say that the electrostatic force existing between a positive ion and one of its coordinated water molecules obeys the simple Coulomb law of electric force. Two such particles cannot be isolated from coulombic forces produced by neighboring ions.

Also, the dielectric constant of the solvent cannot be ignored (Sec. 7-1). However, if we consider the mutual electrostatic energy of an ion and one water molecule in a vacuum, the attractive force follows the simple Coulomb law. Under such simplified conditions the force between the two particles is proportional to the product of the charge on the ion and the electric dipole of the molecule and inversely proportional to the square of the distance between the effective charges. If it is assumed that the ion and the oxygen atom are charged spheres in contact with each other, then the distance between the charges is the sum of the radii of the positive ion and the oxygen atom in the water molecule.

TABLE 5-2 EXTENT OF HYDRATION AS RELATED TO IONIC RADIUS AND POTENTIAL

Ion	Ionic radius, Å	Ionic potential, charge/radius	Extent of hydration
Cs ⁺	1.69	0.59	May not be hydrated
Rb ⁺	1.48	0.68	
K ⁺	1.33	0.75	
Na ⁺	0.95	1.05	Loosely hydrated
Ba ⁺⁺	1.35	1.48	
Li ⁺	0.60	1.70	Definitely hydrated
Sr ⁺⁺	1.13	1.78	
Ca ⁺⁺	0.99	2.00	
Mg ⁺⁺	0.65	3.1	Strongly hydrated
Al ³⁺	0.50	6.0	
Be ⁺⁺	0.31	6.5	

In comparing binding forces of various cations in hydrates the radius of the oxygen atom and the electric dipole charge in the water molecule can be considered as constants. Therefore, in predicting stability of a hydrate, the charge of the central ion and its radius are most significant. As a general rule, stable hydrates are formed by those ions with large charges and small radii.

Since ions such as cesium, rubidium, and potassium are comparatively large with small charges, they are either loosely hydrated or not hydrated at all. Conversely the aluminum ion is small in size with a large electric charge and, as a result, is strongly hydrated in water solution. Table 5-2 shows a comparison of typical ions, isoelectronic with the inert gases, as to their ionic radii, ionic potential, and extent of hydration.

As previously stated, the number of water molecules that are oriented around the central ion is the coordination number of the hydrated ion and is dependent upon the size of the ion. The determination of absolute

hydration numbers is still in the experimental stage, but it is obvious that a small ion, such as the beryllium ion, has a smaller coordination number than a larger ion, as, for example, the barium ion.

5.5 Complexes Resulting from the Formation of Coordinate Bonds.

The coordinate bond is also called the *semipolar bond* because such a bond appears to be partly ionic and partly covalent. This bond may be considered as consisting of an electron pair as in a covalent linkage, but the electron pair is furnished, according to the Sidgwick theory, by one atom or ion in a donor-acceptor relationship. Ions which are isoelectronic with the inert gases do not form the "Werner-type" complexes with their characteristic coordinate linkages. Instead these ions may form hydrates due to electrostatic forces, and there is little evidence that the coupling in such compounds is brought about by the completion of incomplete electronic orbitals.

Ions of the transition elements have a tendency toward the formation of complexes containing coordinate bonds, and these complexes are apparently more stable than those formed by electrostatic forces. As a general rule the radii of the transitional metal cations are less than the radii of those cations which are isoelectronic with the inert gases. This may account, in part, for the greater stability of the transition-ion complexes. An examination of the electronic orbitals of the first transition elements, with atomic numbers 21 to 30, shows that these elements, with the exception of copper and zinc, have incomplete $3d$ orbitals, which are progressively filled in passing through the range of these elements. In general an atom or ion entering into chemical reaction tends to add a sufficient number of electrons to fill incomplete orbitals, within spatial limitations. Ions of the transition elements may accept electrons in pairs from donor atoms. According to Pauling¹ the inner $3d$ orbitals of the transition elements have about the same energy as the $4s$ and $4p$ orbitals of the valence shell, and if they are not completely occupied by unshared electron pairs, they play a very important part in bond formation.

The formation of complex ions by coordinate bonds appears to follow two general rules:

1. The central ion tends to accept electrons to fill incomplete stable orbitals, and each completed orbital contains a pair of electrons of opposite spins.
2. The central ion tends to accept sufficient coordinated molecules or ions to produce a symmetrical structure of molecules packed around the central ion. This structure may be planar, tetrahedral, octahedral, or cubic.

¹ Linus Pauling, "The Nature of the Chemical Bond," p. 93, Cornell University Press, Ithaca, N.Y., 1940.

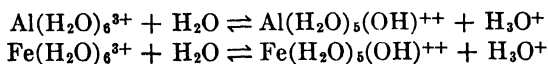
The tendency to attain the inert gas structure, with completed subshells, is significant but not always possible. In some cases the electron shells of inert gases are attained. In other elements which form complexes the total number of electrons either may not attain or may even exceed the number in the inert gas shell. Examples illustrating these various electron shells are given in Table 5-3.

TABLE 5-3 VARIABILITY OF ELECTRON SHELLS IN COMPLEX IONS OF TYPICAL TRANSITION ELEMENTS

Element	Atomic number	Electrons lost in ion formation	Electrons gained in coordination	Total shell
Co(ic)	27	3	12	36
Zn	30	2	8	36
Pt	78	4	12	86
Cr	24	3	12	33
Fe(ic)	26	3	12	35
Ni	28	2	12	38

The production of hydrated ions by the transition elements is a more complicated process than for simple ions with inert gas structures. In the hydrated aluminum ion, which has an inert gas structure, the binding force that produces the complex is an electrostatic one obeying Coulomb's law of electric force. In a hydrated ion of a transition element not only is an ion-dipole bond possible, but there is also the tendency toward coordinate bond formation to fill incomplete stable orbitals of the central ion. Since two processes may be involved in the formation of a hydrated transition ion, it would seem probable that such an ion should be more stable than a hydrated ion in which only ion-dipole forces are in operation. Such a comparison necessarily assumes that the ions are approximately the same size and have equal charges.

An index of the strength of the bond between the central ion and a coordinated water molecule is the ease with which a proton is lost from the complex. The effect of two hydrated ions on the pH of their respective aqueous solutions is indicated in Table 5-4. The ionization equilibria through which protons are produced may be written as follows:



If it is assumed that protons split off more easily from strongly hydrated ions, then the magnitude of the acid constants of these ions should represent their relative stabilities. This assumption must be regarded as speculative since the determination of acid constants of hydrated-ion

234 Fundamental Concepts of Inorganic Chemistry

acids is still in the experimental stage. In Table 5-4 are given two examples of such constants as have been determined.

TABLE 5-4 ACID CONSTANTS FOR TWO DIFFERENT TYPES OF HYDRATED IONS

Ion	Electronic structure	Radius, Å	Acid constant
$\text{Al}(\text{H}_2\text{O})_6^{3+}$	Inert gas structure	0.50	1.4×10^{-5}
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	Incomplete 3d orbitals	0.60	6×10^{-3}

5-6 Magnetic Criterion for Type of Binding. Singly occupied electronic orbits may be detected by measuring the magnetic moments of various ions in aqueous solution. An electron spinning about its own axis and an electron revolving in an orbit are equivalent to an electric current in a circuit. Electrons so described behave as micromagnets and as such possess magnetic moments. The total magnetic moment of an electron is therefore dependent on the spin quantum number s and the orbital-revolution quantum number l . In a completed orbital the magnetic moments of the two coupled electrons compensate for each other, since they have opposite angular momenta as predicted by the Pauli exclusion principle; thus only atoms and ions with incomplete electronic levels are paramagnetic. Substances which are paramagnetic, when placed in a magnetic field, have a greater magnetization than in a vacuum and tend to crowd lines of force together. Magnetic measurements therefore provide a means of detecting the presence of unpaired electrons in atoms, ions, or molecules.

In the transition metal ions the incomplete electron shells are the two outermost shells. In these ions the contribution to the total magnetic moment by the orbital angular momentum may be neglected, since this component is largely canceled by the interaction with outer ions in solution or in crystals. Hence only spin magnetism need be considered because this moment is unaffected by the electric field of the ions but does respond to a magnetic field. In the ions of the transition elements the 3d shell contains five stable orbitals. In passing from vanadium to copper the first five electrons enter one into each of these five orbitals to produce singly occupied orbits. Above five, the additional electrons go into orbitals already containing one electron to form paired electrons with opposed spins. Consequently the number of uncoupled electrons rises to five and falls to zero as the 3d shell is completed. Table 5-5 indicates values in magnetons (the natural unit of magnetic moment) for the magnetic moments of the transition metal ions in solution as compared with the number of unpaired electrons in these ions.

Magnetic data may serve to distinguish between ionic and covalent

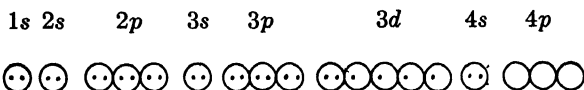
bonding. The transition metals form many octahedral complex ions (in such an ion the six coordinated particles are arranged around the central ion to produce the spatial structure of an octahedron), and magnetic measurements indicate that in some of these complexes the bonding is ionic and in others covalent. For example, the magnetic moment of the ion $\text{Fe}(\text{CN})_6^{3-}$ indicates the presence of one unpaired electron,

TABLE 5-5 MAGNETIC MOMENTS OF VARIOUS IONS IN AQUEOUS SOLUTION

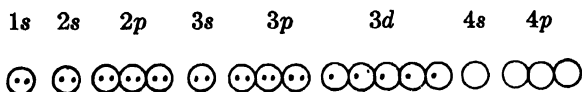
Ion	Number of 3d electrons	Number of unpaired electrons	Moment, magnetons	
			Calculated	Observed
$\text{K}^+, \text{Ca}^{++}, \text{Sr}^{++}, \text{Ti}^{4+}$	0	0	0 00	0.00
$\text{Ti}^{3+}, \text{V}^{4+}$	1	1	1 73	1.7
V^{3+}	2	2	2 83	2 4
$\text{V}^{++}, \text{Cr}^{3+}$	3	3	3 88	3.8-3.9
$\text{Cr}^{++}, \text{Mn}^{3+}$	4	4	4 90	4.8-4.9
$\text{Mn}^{++}, \text{Fe}^{3+}$	5	5	5 92	5.9
$\text{Fe}^{++}, \text{Co}^{3+}$	6	4	4 90	5.3
Co^{++}	7	3	3 88	5.0-5.2
Ni^{++}	8	2	2 83	3.2
Cu^{++}	9	1	1 73	1.9-2 0
$\text{Cu}^+, \text{Zn}^{++}, \text{Ga}^{3+}$	10	0	0 00	0 00

whereas the magnetic moment of the FeF_6^{3-} ion indicates five unpaired electrons. Obviously the bonding in the first complex is covalent, and in the second it must be ionic. This conclusion is reached by examining the distribution of electrons in the ferric and ferricyanide ions.

The iron atom consists of a nucleus surrounded by successive shells of planetary electrons having in them 2, 8, 14, and 2 electrons, respectively. The energy levels and orbitals of the iron atom may be indicated as

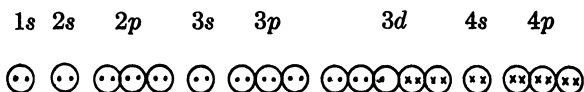


Each circle represents an orbital which may contain a pair of electrons of opposite spins, the electrons being signified by dots. This representation indicates that the iron atom has four unpaired electrons in the 3d orbitals. In forming the ferric ion the iron atom loses its two 4s electrons and one 3d electron, thereby producing an electronic structure containing five singly occupied 3d orbitals, which may be indicated symbolically as



236 Fundamental Concepts of Inorganic Chemistry

Therefore, when the ferric ion accepts 12[—] electrons (indicated by small crosses) from six cyanide ions to form six covalent bonds, the resulting ion $\text{Fe}(\text{CN})_6^{3-}$ contains only one unpaired (3d) electron,



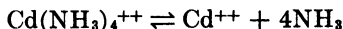
In this ion six stable 3d, 4s, and 4p orbitals are completed in attaining the octahedral structure.

In the case of the FeF_6^{3-} ion the presence of five singly occupied orbitals indicates that the electronic distribution is the same as in the simple ferric ion. Thus the bonding is ionic, in which the fluoride ions are held in the octahedral structure by electrostatic forces.

FACTORS AFFECTING THE STABILITIES OF COMPLEX IONS AND COORDINATION COMPOUNDS

The strength of the linkage between the constituent ions or molecules within a complex varies widely. In a concentrated solution cobaltous ions react with thiocyanate ions to give the blue complex ions with a formula of $\text{Co}(\text{CNS})_4^-$, but this complex is broken down upon dilution with water because of the lesser activity (Sec. 5·7) of the thiocyanate ion. On the other hand the complex ferrocyanide ion $\text{Fe}(\text{CN})_6^{4-}$ in water solution will not give a test for the ferrous ion with the most sensitive reagents. These two examples represent extremes in terms of binding forces in complex compounds. Between these two extremes are many complexes which dissociate in water solution to such a degree that the extent of dissociation may be determined quantitatively.

From the equilibrium reaction of a complex dissociating into its components is obtained a constant which is similar to an ionization constant. However, this constant is usually referred to as a *dissociation constant*, or, less frequently, as a *stability constant*. In the case of the cadmium-ammonia complex, the equilibrium reaction¹ is



and the equilibrium expression for this reaction is

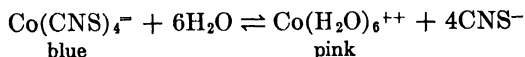
$$\frac{[\text{Cd}^{++}][\text{NH}_3]^4}{[\text{Cd}(\text{NH}_3)_4^{++}]} = 2.5 \times 10^{-7}$$

where the value 2.5×10^{-7} is the dissociation constant of the complex.

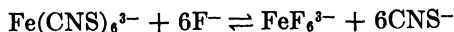
¹ The reader should keep in mind that the dissociation of $\text{Cd}(\text{NH}_3)_4^{++}$ occurs in a stepwise fashion.

However, except for a statement as to the existence of quantitative relationships in complex-ion dissociation, this aspect is not pertinent to the present discussion. On the other hand we are interested in the various factors which determine the stability of a coordinated complex. A few of the more important of these factors are summarized in the following sections.

5-7. Concentration. Lattice complexes consisting of certain double salts and alums, as, for instance, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, are complex substances only in the solid state, since they break down in water solution into simpler substances. Other complexes may exist in water solution only in the presence of a high concentration of the coordinating particles. In such cases, apparently, the water molecules have greater coordinating tendencies than the molecules or ions originally present. An illustration of this behavior is the interaction of the cobaltous ion with a high concentration of thiocyanate ions to produce the blue complex ion $\text{Co}(\text{CNS})_4^-$. Upon dilution with water the blue complex is destroyed, and there appears the characteristic pink color of the hydrated cobaltous ion $\text{Co}(\text{H}_2\text{O})_6^{++}$. Upon further addition of the thiocyanate ion the blue color reappears. This behavior would indicate a competition between the thiocyanate ion and the water molecule in the production of the cobalt complex. The equilibrium reaction may be written as



Another competition between coordinating particles involving concentration factors is that between the CNS^- ion and the F^- for the Fe^{3+} ion. The thiocyanate ion reacts with the ferric ion to produce a dark reddish-brown complex ion with the formula $\text{Fe}(\text{CNS})_6^{3-}$. The addition of excess fluoride ions to the colored complex converts it to a colorless complex with the formula FeF_6^{3-} . Upon the addition of more thiocyanate ions the colored complex reappears. The equation for the equilibrium reaction is



5-8 Nature of the Central Ion. We have already stated (Secs. 5-4 and 5-5) that as a general rule ions of the transition elements form more stable complexes than do those ions which are isoelectronic with the inert gases. Furthermore, for those complexes containing ion-dipole linkages, the size of the central ion and the magnitude of its charge largely determine the stability of the complex which may be formed.

A number of attempts have been made to ascertain the effect of the central ion on the stability of a coordinated complex. These investigations have endeavored to develop a stability sequence for the common

238 Fundamental Concepts of Inorganic Chemistry

cations, or, in other words, a table of the cations listing the order of their tendencies to form coordination compounds. The results of these attempts have been somewhat inconclusive, inasmuch as coordinating tendency depends not only upon the nature of the central ion but also upon the coordinating agent. However, a compilation of the various results indicates that the stability sequence for a few of the divalent cations, regardless of the coordinating agent involved, is in the order given in Table 5-6. The property of the central ion from which this sequence arises is not readily apparent, although it does roughly parallel the order of the second ionization potential for these atoms. Hence the correlation could possibly indicate the sequence in acceptor properties of the central ion for the electrons of the coordinating groups.

TABLE 5-6 STABILITY SEQUENCE FOR A FEW DIVALENT CATIONS IN COORDINATED COMPLEXES

Stability sequence	Pd ⁺⁺	Cu ⁺⁺	Ni ⁺⁺	Co ⁺⁺	Zn ⁺⁺	Cd ⁺⁺	Fe ⁺⁺	Mn ⁺⁺	Mg ⁺⁺
Second ionization potential.....	19.8	20.3	18.2	17.3	17.9	16.8	16.2	15.7	15.0

5-9 Nature of Coordinating Groups. According to Sidgwick any coordinating group must attach itself by sharing with the central ion a "lone" pair of electrons. Furthermore, he states that all such groups which are capable of entering into a complex in this way can be shown to possess the necessary lone pair. However, there is a considerable difference in the ease with which coordinating groups attach themselves to the central ion, and, consequently, there is also a difference in the stabilities of the coordination compounds which are produced.

Since only the more electronegative elements can act as electron donors, coordinate bonds are largely limited to atoms of carbon, nitrogen, oxygen, sulfur, and the halogens. Donor groups containing these atoms, and the resulting complexes, are listed in Table 5-7. However, many complexes, particularly those formed with the fluoride ion, are largely ionic in nature rather than covalent.

Owing to the complex nature of coordination compounds it is difficult to assign with any exactness the particular affinity of different coordinating groups for the central ion. In Table 5-7 the related donor groups are listed in the order of their relative stabilities. It must be emphasized that this order is decidedly approximate, and there are probably as many exceptions as there are examples which conform to the order of the stability sequence.

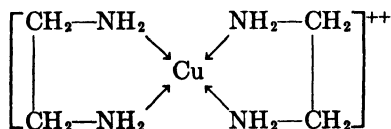
5-10 Cyclization. A complex containing a ring structure results whenever a single group or molecule occupies two or more coordination

positions on the same atom. A cyclic compound of this type is termed a *chelate* from the Greek word *chele*, meaning *claw*. The name is applicable to these ring systems because of the clawlike character of the associating molecule. We shall have occasion to discuss chelate compounds more completely in Secs. 5-14 through 5-19; our present interest is confined to the stabilizing effect apparently resulting from cyclization.

TABLE 5-7 SOME ELECTRON DONORS WHICH MAY ENTER INTO
COMPLEX FORMATION

Donor atom	Donor groups in approximate stability sequence	Complexes formed	Examples
C	CN ⁻ , CO	Cyanide Carbonyl	Cd(CN) ₄ ⁻ Ni(CO) ₄
N	NH ₃ , NO, NO ₂ ⁻	Ammine Nitroso Nitrito	Cu(NH ₃) ₄ ⁺⁺ Co(NH ₃) ₅ NO ⁺⁺ Co(NO ₂) ₆ ³⁻
O	H ₂ O, OH ⁻ , C ₂ O ₄ ⁻ , CO ₃ ⁻	Aquo Hydroxide Oxalato Carbonato	Cr(H ₂ O) ₆ ³⁺ Zn(OH) ₄ ⁻ Fe(C ₂ O ₄) ₂ ³⁻ Co(CO ₃) ₂ ⁻
S	CNS ⁻ , S ₂ O ₃ ⁻ , S ⁻	Thiocyanato Thiosulfate Sulfide	Hg(CNS) ₄ ⁻ Ag(S ₂ O ₃) ₂ ³⁻ SnS ₃ ⁻
Halogen	F ⁻ , Cl ⁻ , Br ⁻ , I ⁻	Fluoride Chloride Bromide Iodide	FeF ₆ ³⁻ CuCl ₄ ⁻ PbBr ₄ ⁻ HgI ₄ ⁻

Groups which are able to occupy two or more coordination positions are usually organic molecules. A typical molecule of this description is ethylenediamine, NH₂CH₂CH₂NH₂, which contains a donor nitrogen atom at both ends of the molecule and, consequently, may attach itself in two coordination positions to a central metal ion. In forming the copper chelate two molecules of ethylenediamine attach themselves to the cupric ion in a caliperlike manner to form two five-membered rings. The structure of this cyclic complex may be indicated as



240 Fundamental Concepts of Inorganic Chemistry

In general a chelated complex is more stable than a complex which is similar but nonchelated. This generality may be verified by examining Table 5-8, in which are listed the stability constants of zinc, cupric, and nickel chelates of ethylenediamine as compared with the corresponding stabilities of the simple amines. An additional proof is the fact that ethylamine, $C_2H_5NH_2$, which possesses only one coordinating group, forms complexes with many of the transitional metals, and these complexes are much less stable than those formed by ethylenediamine with its two coordinating groups.

TABLE 5-8 STABILITY CONSTANTS OF THREE METAL AMMINES*

Complex	Consecutive complexity constants	Log dissociation constant
$Zn(NH_3)_4^{++}$	$k_1k_2k_3k_4$	9.46
$Zn(en)_2^{++\dagger}$	k_1k_2	11.07
$Cu(NH_3)_4^{++}$	$k_1k_2k_3k_4$	12.67
$Cu(en)_2^{++}$	k_1k_2	20.03
$Ni(NH_3)_6^{++}$	$k_1k_2k_3k_4k_5k_6$	6.74
$Ni(en)_3^{++}$	$k_1k_2k_3$	18.61

* J. Bjerrum, *Chem. Revs.*, **46**: 381 (1950).

$\dagger en = NH_2CH_2CH_2NH_2$.

GENERAL TYPES OF COMPLEX IONS

All ions in aqueous solution may be regarded as complex ions. These ions may be hydrates, or the complexes may result from the union of a central ion with other ions, atoms, or molecules. A study of the numerous possible combinations to produce complex ions is beyond the scope of this book. Consequently our discussion will be limited to those complex ions of most common occurrence. One broad classification of complex ions divides them into three general types:

1. Complex ions formed by the union of cations with inorganic molecules. The ammoniates and hydrates are familiar examples of this type of complex.

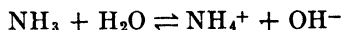
2. Complexes formed by the union of cations with inorganic anions in which the anions are usually in excess of the number to satisfy the electrovalence of the cations. Among the many anions which, in excess, may produce such complex ions are the cyanide, hydroxide, thiocyanate, sulfide, thiosulfate, and halide ions.

3. Complexes resulting from the union of inorganic cations with organic anions or molecules.

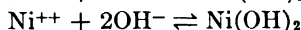
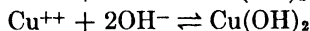
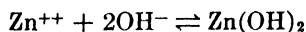
5-11 Complex Ions Formed by the Union of Cations with Inorganic Molecules. Hydrated Ions. The majority of ions are hydrated to some

extent in aqueous solution. The stability of such ions varies with many factors, as has been explained in the preceding pages. Familiar examples of these ions are the hydroxium ion H_3O^+ , the hydrated aluminum ion $\text{Al}(\text{H}_2\text{O})_6^{3+}$, the hydrated chromic ion $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and the hydrated beryllium ion $\text{Be}(\text{H}_2\text{O})_4^{++}$.

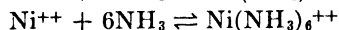
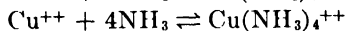
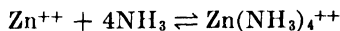
Ammoniates. Many cations form coordination compounds with ammonia. The ammonium ion NH_4^+ results from the union of an ammonia molecule with a proton,



This equation indicates that a water solution of NH_3 will also contain hydroxide ions. In low concentrations of ammonia, the hydroxide ions may produce the first reaction with a cation,



In the presence of excess ammonia the hydroxide precipitates are dissolved with the formation of complex ions, which, although soluble, yield an even lower concentration of metallic ions than the hydroxide.

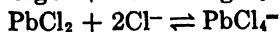
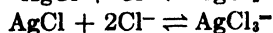
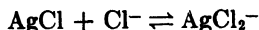


Other frequently encountered ammonia complexes are $\text{Ag}(\text{NH}_3)_2^+$, $\text{Cd}(\text{NH}_3)_4^{++}$, and $\text{Co}(\text{NH}_3)_6^{3+}$.

The extent to which a hydroxide or an ammonia complex is formed with a cation depends not only upon the concentration of ammonia but also upon the stability of the complex that is produced. Certain cations, e.g., aluminum and iron, always precipitate as hydroxides with ammonia because the stabilities of the ammonia complexes are insufficient to put the hydroxides into solution.

5.12 Complex Ions Formed by the Union of Cations with Inorganic Anions. The majority of anions may enter into complex formation with certain cations. Usually these cations are low in the reactivity series, consequently showing a marked tendency to form coordinate bonds.

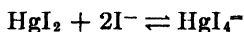
Halide Complexes. Insoluble chlorides are somewhat soluble in a high concentration of chloride ions. The composition of the soluble complex ion which is formed depends upon the concentration of the excess chloride ion. For example,



242 Fundamental Concepts of Inorganic Chemistry

Among the other complex chloride ions which have been identified are CuCl_2^- , CuCl_4^- , HgCl_4^- , AuCl_4^- , PtCl_6^- , SnCl_6^- , CdCl_4^- , and CoCl_6^{3-} .

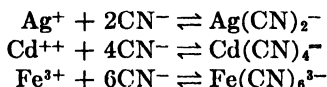
The bromide and iodide ions form complex ions similar to the complex chloro ions. One familiar complex iodide ion is formed by the solvent action of excess iodide ions upon mercuric iodide,



Other bromide and iodide complexes most commonly encountered are AgBr_2^- , PbBr_4^{2-} , PbI_4^{2-} , BiI_4^- , and SbI_4^- .

The fluoride ion is the most effective complexing agent among the halides, and as might be expected, the fluoro complexes are usually extremely stable. A few of the most common examples are SiF_6^{2-} , FeF_6^{3-} , AlF_6^{3-} , and BF_4^- .

Cyanide Complexes. The cyanide, thiocyanate, and thiosulfate ions are sometimes referred to as *pseudohalogens*, since their chemical reactions resemble those of the halides. Many insoluble cyanides are soluble in excess cyanide ions owing to the formation of complex cyanide ions. Three such cyanides are silver, cadmium, and ferric cyanides.



A few of these complexes, such as the ferrocyanide and ferricyanide ions, are so stable that they are only slowly decomposed in strong-acid solutions.

Other cyanide complexes of interest include $\text{Cu}(\text{CN})_3^{2-}$, $\text{Zn}(\text{CN})_4^{2-}$, $\text{Hg}(\text{CN})_4^{2-}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Ni}(\text{CN})_4^{2-}$.

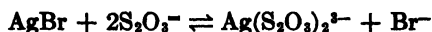
Thiocyanate Complexes. As might be expected, the thiocyanate complexes are somewhat analogous to complex halogen ions.

Insoluble silver thiocyanate and mercuric thiocyanate are soluble in excess thiocyanate ions.



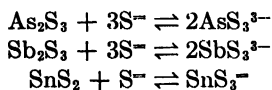
The ferric ion and thiocyanate ion may combine to produce colored complex ions varying in composition from $\text{Fe}(\text{H}_2\text{O})_6\text{CNS}^{++}$ to $\text{Fe}(\text{CNS})_6^{3-}$.

Thiosulfate Complexes. Silver chloride and silver bromide dissolve in sodium thiosulfate solution to form a stable complex silver thiosulfate anion. This reaction is important in photography. After the developing of a photographic film the sodium thiosulfate solution is used to dissolve away the silver halide not reduced by the developer. The equation of this dissolving action is



Other complex thiosulfate ions are $\text{Hg}(\text{S}_2\text{O}_3)_2^-$, $\text{Bi}(\text{S}_2\text{O}_3)_3^{2-}$, $\text{Cu}_2(\text{S}_2\text{O}_3)_2^-$, and $\text{Pb}(\text{S}_2\text{O}_3)_2^-$.

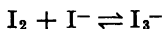
Sulfide Complexes. The sulfides of arsenic, antimony, and tin are soluble in excess sulfide ions owing to the formation of stable complex ions. This complex formation may be utilized in separating these three sulfides from the other sulfides of Cation Group II in the classical scheme of qualitative analysis. The production of these soluble complex ions is represented by the following equations:



A very high concentration of sulfide ions will dissolve mercuric sulfide to produce the mercuric sulfide complex, as follows:



Homoatomic Anions. These complexes result from the union of neutral atoms or molecules with their ions to form soluble complex anions. Two familiar examples of homoatomic anions are the tri-iodide ion and the sulfur-sulfide ion. Iodine molecules dissolve only slightly in water but are readily soluble in potassium iodide solution. The equation for the reaction which produces this increased solubility is

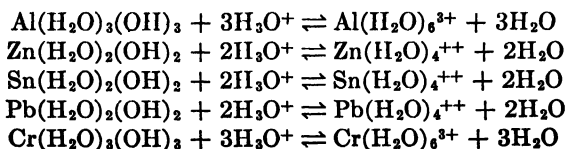


Ammonium polysulfide is a reagent that will dissolve the sulfides of arsenic, antimony, and tin. Consequently it is sometimes utilized in qualitative analysis to separate Cation Group II into subgroups in which these sulfides are dissolved from the other cations which make up the group. This reagent is prepared by dissolving sulfur in ammonium sulfide solution, according to the following equation:



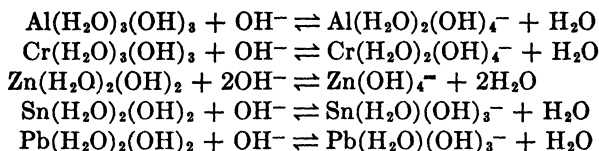
The reaction is not limited to the formation of the diatomic ion. There is considerable evidence that the ions S_3^{2-} , S_4^{2-} , and S_6^{2-} may also be formed.

Hydroxide Complexes (Amphoteric Hydroxides). Certain insoluble hydroxides combine with acids and bases to form salts. Such hydroxides are referred to as *amphoteric hydroxides* because of their dual nature in acid-base reactions. Equations representing some of the most familiar hydroxides of this type acting as acids are

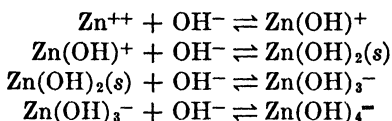


244 Fundamental Concepts of Inorganic Chemistry

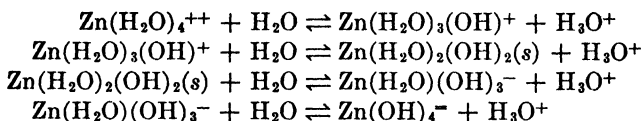
Although the reactions of insoluble hydroxides with bases are also acid-base reactions, such reactions proceed because of the formation of stable hydroxide complex ions. These reactions may be represented as



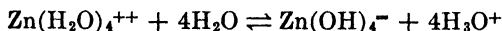
The reactions of the zinc ion to form a series of hydroxide complexes may be represented as either complex-ion formations or acid-base reactions. From the viewpoint of complex-ion formation the following equations are illustrative:



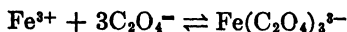
Another interpretation of the behavior of an amphoteric hydroxide is to consider such a hydroxide as an intermediate stage in the hydrolysis of a hydrated ion. The coordinated water molecules of the hydrated ion may be replaced by hydroxide ions. To illustrate this point of view, consider the hydrated zinc ion as an acid with four replaceable protons.



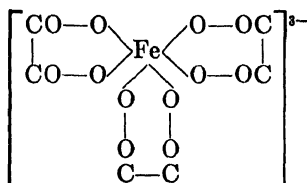
The four stepwise equations may be combined into one equation, as



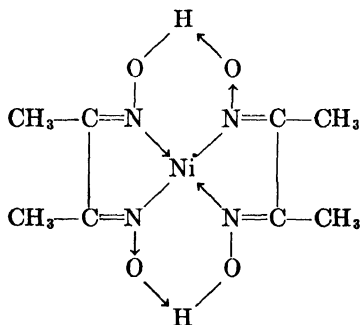
5-13 Complex Ions Formed by the Union of Cations with Organic Anions or Molecules. Certain inorganic cations may form coordination compounds with specific organic ions or organic molecules. If the coordination groups are organic ions, the complex produced is usually an anion and is soluble in water. Such an electrolyte is produced when the ferric ion reacts with oxalate ions. A simple equation for the formation of this complex is



The structure of the complex ion may be represented as



If the coordinating ion or molecule is attached to the central group by two bonds in such a manner as to produce a closed ring, the resulting compound is a chelate. Complexes incorporating ring structures, particularly where there are five or six atoms in the ring, are generally quite stable. One of the most familiar chelate compounds, used in analytical chemistry for the determination of nickel, is produced when the nickel ion reacts with dimethylglyoxime. The structure of the complex produced by this reaction may be represented as



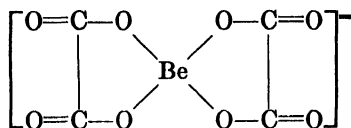
In this compound the nickel atom has a coordination number of 4 and is attached to two molecules of dimethylglyoxime by two covalent bonds and two coordinate bonds.

The hundreds of known chelate compounds have been classified in many ways. These compounds are of sufficient importance for them to be discussed more completely in Secs. 5-14 through 5-19. At present it seems worthwhile to mention a simple method of classification, used by several writers, in which chelates are classified according to the nature of the links that close the ring, or rings, of the cyclic compounds. In respect to the nature of the linkages chelates may be classified into three types.

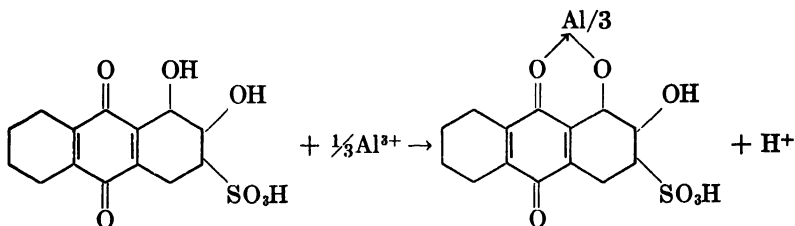
Type A. Complexes in which the cation is combined through covalent bonds only. Rings of this type are formed by the replacement of two hydrogen atoms by the metallic cation. Usually the two hydrogen

246 Fundamental Concepts of Inorganic Chemistry

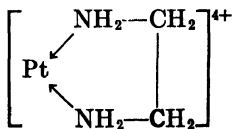
atoms split from hydroxyl or carboxyl groups, where the latter are so positioned as to produce five-membered rings. A typical example is the complex formed between the beryllium and oxalate ions.



Type B. Complexes in which the cation is combined through both covalent and coordinate bonds. Complexes of this type are nonelectrolytes and are insoluble in water. One such complex, nickel dimethylglyoxime, has already been given. Another example is the chelate structure produced by the reaction of the aluminum ion with alizarin red S. In this compound three molecules of the dye combine with one aluminum ion to form a red precipitate whose partial structure may be indicated as



Type C. These are complexes in which the cation forms only coordinate bonds in closing a ring. The diamines which have two amine groups, each of which may donate electrons, tie up certain cations with only coordinate linkages. Such a complex is formed by the union of ethylene diamine with platinic chloride.



CHELATES

Although the first chelate was recognized and described by Werner, the development of chelate chemistry has taken place almost entirely within recent years. However, chelation is nothing more than a special form of complex formation, and what has been said concerning simple complexing applies equally well to chelate formation. On the other hand the

majority of chelate compounds result from the linking of metal atoms to organic molecules; consequently this branch of chemistry might be incorporated as well in the field of organic chemistry as in that of inorganic chemistry. Moreover the information relating to chelate chemistry has become so extensive that it is impossible to present more than an outline summary of the topic in this book.

5.14 The Ring Structure of Chelates. A chelate possesses a cyclic structure arising from the union of a metal ion with an organic or inorganic molecule, with two or more points of attachment to produce a closed ring. Usually chelate rings contain five or six members, including the metal ion, since these numbers apparently result in a reduced strain and are consequently more stable. Where either a five- or a six-membered ring may be formed, invariably (unless double bonds are involved) the five-membered ring is produced, indicating that this is the most stable ring that can be closed. The tendency to form rings of low strain parallels the formation of carbon rings in organic chemistry.

As was stated in Sec. 5.13, rings may be closed by the formation of covalent linkages, or coordinate bonds, or by a combination of the two. In fact the nature of the linkages has been used as a basis for the classification of chelate compounds. Covalent bonding is produced by the replacement of a proton in an organic group. Functional groups of this type are sometimes called *acidic* groups because of the fact that hydrogen may be replaced from them. The most common examples of these groups are —COOH (carboxyl), $\text{—SO}_3\text{H}$ (sulfonic), —OH (enolic hydroxyl), and =NOH (oxime). Coordinate linkages, without the replacement of hydrogen, are formed by the donation of an electron pair. The most common functional groups which contain donor atoms are —NH_2 (primary, secondary, and tertiary amines), =NOH (oxime), —OH (alcoholic hydroxyl), =CO (carbonyl), and —S— (thioether). Chelation will therefore be favored when any of the foregoing groups occur in the 1,4 or 1,5 positions of an organic molecule.

5.15 Classification of Chelates. The three types of chelates given in Sec. 5.13 refer to those cyclic compounds in which the metallic ion is attached to the coordinating agent by only two linkages. With the discovery of compounds in which the metal atom is linked to the organic molecule through three or more groups, it became necessary to devise another system of classification. It was G. T. Morgan who first coined the name *chelate*, from the Greek word for *claw*. Later, as other compounds with more than two points of attachment to the central ion were discovered, Morgan originated for these compounds the names *tridentate* and *quadridentate*, which literally mean *three-toothed* and *four-toothed*. Actually quinquidentate and sexadentate compounds are possible, although very few have been knowingly recorded as such.

248 Fundamental Concepts of Inorganic Chemistry

Since polydentate molecules may be attached to the central metal atom through two kinds of functional groups, acidic and coordinating, to form covalent and coordinate linkages, the logical classification of chelate compounds should follow the number and kind of attachments involved. Such a classification has been developed¹ and is presented in outline form:

A. Bidentate

1. Two acidic groups
2. One acidic group, one coordinating group
3. Two coordinating groups

B. Tridentate

1. Three acidic groups
2. Two acidic groups, one coordinating group
3. One acidic group, two coordinating groups
4. Three coordinating groups

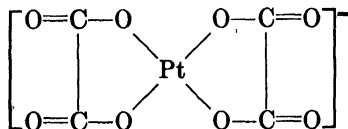
C. Quadridentate

1. Four acidic groups
2. Three acidic groups, one coordinating group
3. Two acidic groups, two coordinating groups
4. One acidic group, three coordinating groups
5. Four coordinating groups

and so on, for quinquidentate and sexadentate.

5.16 The Bidentate Compounds. The Types A, B, and C chelate compounds given in Sec. 5.13 were bidentate compounds. However, to emphasize the system of classification for these compounds, additional illustrations are offered as follows:

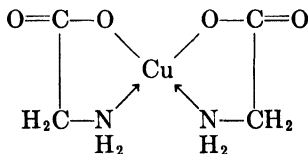
Two Acidic Groups Forming Attachments through Covalent Bonding. A compound typifying these linkages is produced by the interaction of the platinic and oxalate ions.



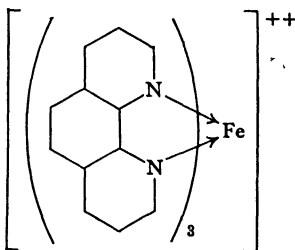
One Acidic Group and One Coordinating Group. The cupric ion reacts with glycine to produce copper glycinate, in which each glycine molecule

¹ H. Diehl, *Chem. Revs.*, **21**: 39 (1937).

is attached to the copper atom by one covalent bond and one coordinate bond.



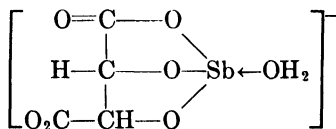
Two Coordinating Groups. Orthophenanthroline is a heterocyclic organic compound having two ring nitrogen atoms. This substance forms a complex ion with the ferrous ion in which three molecules of the orthophenanthroline are each attached to one ferrous atom by two coordinate linkages. The formula for this chelate may be indicated as



The ferrous-orthophenanthroline complex is a useful redox indicator.

5.17 The Tridentate Compounds. According to the classification given in Sec. 5.15 four classes of tridentate compounds are possible. Members of all these classes are known, although the evidence of a tridentate complex formed by the attachment of three acidic groups is somewhat in doubt.

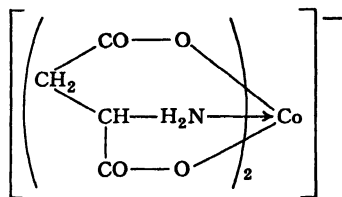
Three Acidic Groups. Tartar emetic, used in medicine and as a mordant, is obtained by boiling antimony oxide and potassium acid tartrate. The formula which has been assigned to the soluble complex ion indicates that the antimony atom is attached to the tartrate ion by the splitting off of three hydrogen atoms to form three covalent linkages.



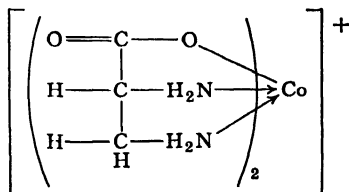
Two Acidic Groups and One Coordinating Group. Aspartic acid combines with trivalent cobalt to form a water-soluble tridentate compound.

250 Fundamental Concepts of Inorganic Chemistry

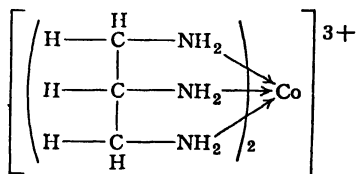
The structure given to this complex ion is



One Acidic Group and Two Coordinating Groups. The cobaltic ion interacts with diaminopropionic acid to give a tridentate compound in which each molecule of the acid is attached to the cobalt atom by two coordinate linkages and one covalent bond. The formula for this chelate is



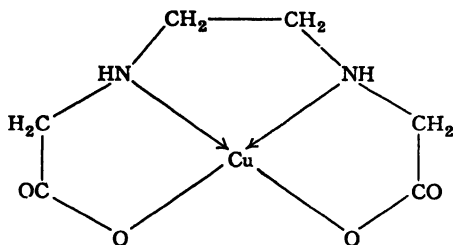
Three Coordinating Groups. Triaminopropane combines with a number of transitional metallic ions to produce a chelate, in which one molecule of the triaminopropane occupies three coordination positions about the metallic atom. The structure for the cobaltic tridentate compound formed with this organic molecule is



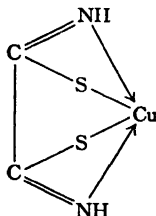
5-18 Quadridentate and Sexadentate Compounds. Very few polydentate chelating agents beyond those capable of filling tridentate groupings are known. To fill four or more coordination positions requires specialized geometrical conditions in order to produce a strain-free structure, and such conditions do not occur in many molecules. Only two of the possible five classes are known.

Two Acidic Groups and Two Coordinating Groups. Ethylenediamine-acetic acid reacts with the cupric ion to produce a quadridentate grouping

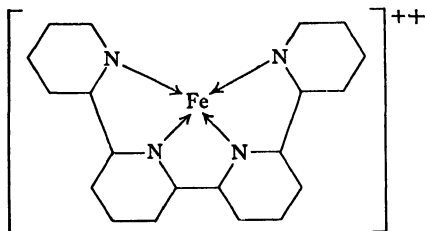
containing two covalent bonds and two coordinate linkages. The structure of this compound is



Rubeanic acid (dithiooxamide) also reacts with the cupric ion to give a chelate which may be a quadridentate compound. A doubtful structure which has been assigned to this complex is



Four Coordinating Groups. Tetrapyridyl reacts with certain bivalent transition metals, such as Fe^{++} , Co^{++} , Ni^{++} , Cu^{++} , and Zn^{++} , to form a quadridentate compound in which the organic molecule is attached to the metal by four coordinate linkages. In the case of the ferrous compound the structure of the chelate is

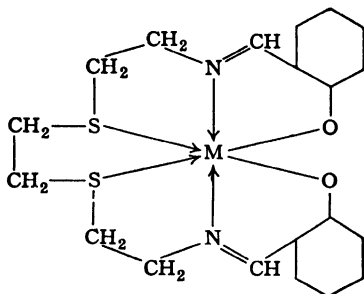


Sesadentate Chelate Compounds. Dwyer and Lions¹ have prepared several organic molecules containing six groups (two acidic and four coordinating) capable of attaching themselves in six octahedral positions of the coordination sphere of a central metallic atom. One of these molecules, 1,8-bis-salicylideneamino-3,6-dithiooctane, reacts with zinc, nickel,

¹ F. P. J. Dwyer and F. Lions, *J. Am. Chem. Soc.*, **72**: 1545 (1950).

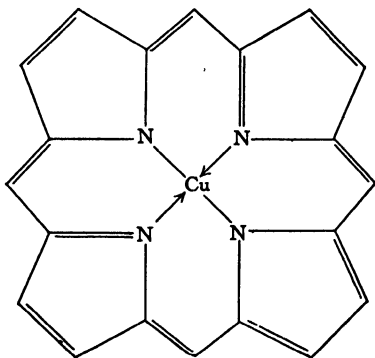
252 Fundamental Concepts of Inorganic Chemistry

copper, or cobalt to form a chelate compound with the following possible structure:



A molecule containing polydentate groups must necessarily be able to wrap itself around the central atom in order to attain the maximum coordination positions.

5.19 The Importance of Chelates. The field of chelate chemistry is relatively new, and most of the explorations in this field have been in recent years. Among the earlier important investigations were those of Willstätter and H. Fischer, who established the general structures of chlorophyll and hemin. Chlorophyll, the green pigment of plants, contains two closely related colored substances, both of which are magnesium chelates containing four pyrrole nuclei united by methylene groups to form the porphyrin ring. Hemin, the red coloring matter of the blood, is an iron chelate. This compound also contains a porphyrin ring with four pyrrole nuclei and is structurally quite similar to chlorophyll. It is interesting that among the invertebrates, particularly in crustaceans and mollusks, the central atom is copper in place of iron. Other oxygen carriers in the blood of various invertebrates are the chelate compounds of the elements manganese and vanadium. The parent unsubstituted porphyrin ring has been synthesized by Fischer, and the copper compound has the structure



Chelating agents are becoming of increasing importance in analytical chemistry. In qualitative analysis nickel, magnesium and aluminum ions are usually identified by the formation of stable, highly colored chelates. In gravimetric analysis magnesium and nickel may be precipitated quantitatively by chelating agents, and in volumetric analysis chelating agents are frequently used as indicators in the titration of certain metal ions.

Among the most important uses of chelating agents is that of water softening. Ion-exchange resins have been developed, based on coordination phenomena, which successively remove both cations and anions from aqueous solution, and the resulting "deionized" water may approach distilled water in purity.

It is beyond the scope of this book to go into the many varied uses of chelating agents. These uses cover a wide range of applications such as medicinals, detergents, antioxidants, dyeing, water softening, enzyme deactivators, etc. An interesting summary of chelating agents and their uses has been compiled by Martell and Calvin.¹ These writers state that chelating agents may be roughly divided into two classes depending on whether they form water-soluble chelates or whether they form metal chelates which precipitate. The former are called *sequestering agents*, which are used in aqueous solution for the effective removal of objectionable metal ions. Not only is this class important in laundering, boiler-scale removal and other similar commercial applications, but chelating agents such as ethylenediamine tetraacetic acid are used to speed the elimination of harmful radioactive metals from the body. Chelates of the second class are largely used for analytical purposes or for solvent extraction. For example, the separation of zirconium and hafnium was a most arduous analytical task until it was discovered that the chelates of the two metals formed with thenoyltrifluoroacetone possess different solubilities in benzene. The distribution coefficients of the two chelates differ by a factor of 20, the Zr having the greater tendency to be extracted. Consequently it is now possible to effect a good separation of these metals by successive extractions of the two ions with thenoyltrifluoroacetone in benzene.

✓ ISOMERISM IN COORDINATION COMPOUNDS

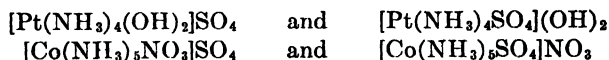
Of frequent occurrence in organic chemistry is the existence of two or more chemical compounds with identical chemical compositions but with different properties. Compounds of this description are called *isomers*, and the structural difference which produce dissimilar properties is referred to as *isomerism*. The phenomenon of isomerism is not limited

● A. E. Martell, and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice Hall, Inc., Englewood Cliffs, N.J., 1952.

254 Fundamental Concepts of Inorganic Chemistry

to the chemistry of carbon compounds but is also found less frequently among inorganic substances. The variety of chemical linkages and complexity of stereochemical relationships which occur in coordination compounds are favorable to those structural arrangements which lead to isomerism. Moreover the multiplicity of molecular arrangements which is found among these compounds produces more types of isomerism than are possible in strictly organic molecules. In the following sections are described various types of isomerism that have been predicted by the Werner theory.

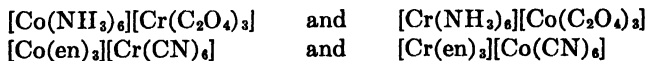
5-20 Ionization Isomerism. As indicated in Sec. 5-2, ions may lose their electrovalent properties and enter into the coordination sphere. This shifting from the outer to the inner sphere is also a transition from an ionic linkage to a covalent bond, with an attendant change in properties of the atoms concerned. Hence it is possible to have two compounds with the same empirical formula, but containing different ionic groupings. For example, the violet bromopentammine sulfate of cobalt with a formula of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ is an ionization isomer of the red sulfatopentammine bromide with a formula of $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$. Both these compounds have the same empirical formula, but the first gives a precipitate of BaSO_4 with BaCl_2 and no precipitate with AgNO_3 and the second gives a precipitate of AgBr with AgNO_3 and no precipitate with BaCl_2 . Other illustrations of ionization isomerism are



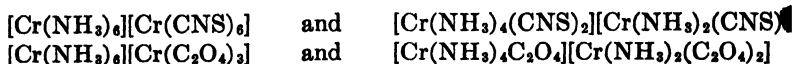
5-21 Coordination Isomerism. In this type of isomerism two compounds of identical composition are made up of different complex ions as a result of different groups being coordinated about the same coordination centers. In the compounds



cobalt occurs in the cation of the first and in the anion of the second, whereas for chromium the situation is reversed. Other examples of coordination isomerism are



Another form of the same type of isomerism may occur when the same metal appears in both cation and anion of two compounds in which there is a different distribution of donor components. Compounds exemplifying this arrangement are



5-22 Polymerization Isomerism. This term is used to describe compounds which have the same stoichiometric composition but whose molecular compositions are multiples of the simplest stoichiometric arrangement. For example, in the three compounds

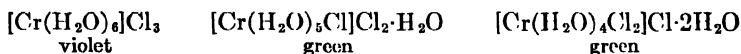


the second and third compounds may be said to be polymers of the first. Actually, in the strict sense of the word, these are not examples of polymerization. Polymerization is usually interpreted as meaning a multiplication of simple molecules. Here we have differences in arrangements as well as a multiplication of molecular weight.

Other compounds illustrating polymerization isomerism are

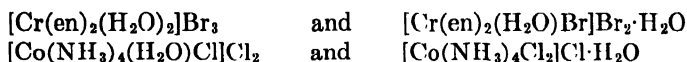


5-23 Hydrate Isomerism. As was pointed out in Secs. 5-4, 5-5, and 5-9, the water molecule is one of the most effective coordinating agents, and as a result there are many aquo complexes. The number of molecules which may enter into the coordination sphere of a metallic ion depends upon various factors and conditions, some of which have already been discussed. At present we are chiefly interested in the fact that the number of such molecules in the inner sphere does vary, and this variation results in the formation of hydrate isomers. For example, there are three different hexahydrates of chromic chloride with an empirical formula of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. One of these hydrates is violet and the other two green in color. All three differ in the number of molecules of water in the coordination sphere. The formulas which have been assigned to these three hydrate isomers are



These compounds differ not only in color but also in their solubilities. Also, as might be predicted from their formulas, silver nitrate can precipitate all the chlorine from the first isomer, two-thirds from the second, and only one-third from the third.

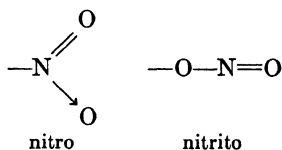
Other compounds in which hydrate isomerism is exemplified are



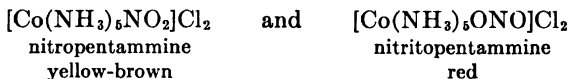
5-24 Salt Isomerism. Isomerism of this type results from two possible methods of linkage of a coordinating group to a central atom. Thus the NO_2 group may be attached as a nitro grouping with pentavalent nitrogen linking itself to the central atom directly, or the group can be attached as a nitrito grouping with trivalent nitrogen linked to the central atom

256 Fundamental Concepts of Inorganic Chemistry

through an oxygen atom. These two groupings may be indicated as

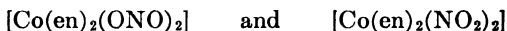


Examples of isomeric forms resulting from these two modes of linkage are



This kind of isomerism was named *salt isomerism* by Werner, although the name is more or less meaningless since it conveys no idea as to the structural characteristics within this type of isomerism. The term *linkage isomerism* seems more appropriate.

Other compounds which illustrate salt isomerism are



STEREISOMERISM

Stereoisomerism is one of the types of isomerism predicted by the Werner theory. Furthermore it is the most widely occurring and consequently the most important of any of the forms of isomerism. Although no attempt will be made to go into the stereochemistry of complex inorganic compounds completely, it seems worthwhile to devote more space to this phenomenon than was apportioned to the discussion of the other types of isomerism.

Stereoisomerism is a form of isomerism in which two substances of the same composition and constitution differ only in the relative positions in space assumed by certain of their constituent atoms or groups. This phenomenon is sometimes called *geometrical isomerism*, inasmuch as two isomers may possess the same geometrical figure but may differ only as to the points of attachment of coordinating groups.

Stereoisomers of compounds with the coordination numbers of 6 and 4 are well known, and in many cases proof of the configurations of these stereoisomers has been established. For the other coordination numbers no isomeric phenomena have as yet been observed to establish definite spatial structures. Hence our discussion will be centered on those stereoisomers of known existence and will omit those of speculative possibilities.

5.25 Stereoisomerism in Octahedral Complexes. The symmetrical arrangement of six coordinating groups about a central atom can be

attained either in a plane configuration, as in a benzene ring, or at the corners of an octahedron. Since the number of isomers which can exist for these two spatial arrangements is different, the number of isomers observed confirm the true configuration. If the spatial arrangement is assumed to be that of a regular hexagon for a compound of the general type (Ma_4b_2), where M indicates the central metal and a and b are different coordinating groups, then three isomers should exist, corresponding to the *ortho*, *meta*, and *para* derivatives of benzene. However, the number

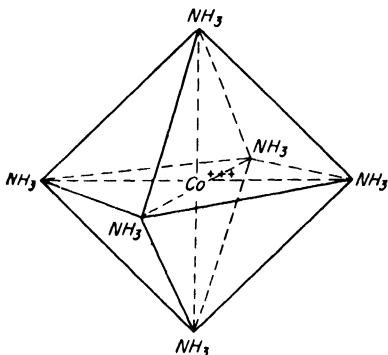


Fig. 5-2 Octahedral configuration in $[\text{Co}(\text{NH}_3)_6]^{3+}$.

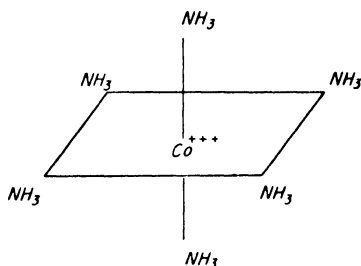


Fig. 5-3 Simplified representation of the octahedral configuration of $[\text{Co}(\text{NH}_3)_6]^{3+}$.

of isomers observed for compounds of this type have always been two; consequently the possibility of a hexagonal configuration may be ruled out. Moreover, since only two isomers are possible for an octahedral arrangement, as indicated in Fig. 5-4, such a α -configuration may be assumed to be the true one.

The packing of atoms and ions in crystal lattices was discussed in Sec. 4-9. It is believed that the components of a crystal behave as closely packed spheres, and the same is probably true for the constituents of a complex ion either in a lattice or in aqueous solution. Any attempt to indicate the arrangement of groups or atoms in isomeric compounds by means of diagrams, such as were used in Sec. 4-9, would be extremely difficult and perhaps confusing. For the sake of simplicity we shall indicate isomeric arrangements in complex ions with the simplest of geometrical figures. By way of illustration the geometric figure for the octahedral arrangement of components in the ion with the empirical formula of $[\text{Co}(\text{NH}_3)_6]^{3+}$ could be represented by Fig. 5-2. However, this figure may be simplified to the form given in Fig. 5-3. The latter type of diagram will be used throughout our discussion to represent a complex ion with an octahedral configuration. Also, in order to obtain even greater simplicity, we shall frequently omit the symbol of the central atom.

No isomerism is possible for a complex of the type $[Ma_5b]$. However, for those complexes of the type $[Ma_4b_2]$ and $[Ma_4bc]$ two isomers are possible. These possibilities are indicated in Fig. 5-4, and experimental findings have justified the prediction of two such isomers.

It may be observed in Fig. 5-4 that the two coordinating groups differing from the others can occur either in the edgewise or in the axial positions. Where one or both of the substituents occur in the edgewise

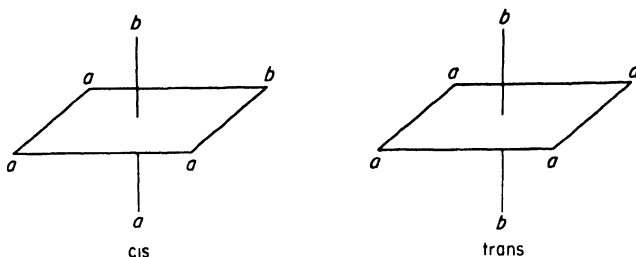


Fig. 5-4 The two isomeric forms of a complex with the general formula $[Ma_4b_2]$.

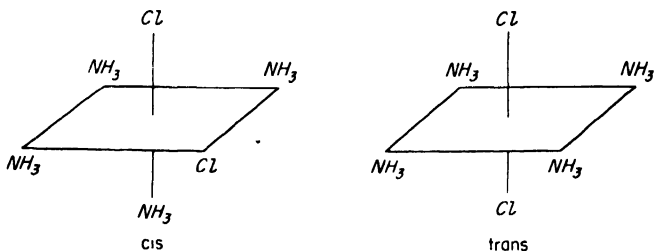


Fig. 5-5 Isomeric configurations of ions produced by the two salts with the formula $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$.

position, the compound is called the *cis* isomer. If the two differing components occur in the axial position, the substance is referred to as the *trans* isomer. Cis-trans isomerism may be exemplified by the two dichlorotetrammine salts of cobalt with the formula $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$. One of these salts is green and the other violet, and they are sometimes called the *praseo* (from the Greek word for *green*) and the *violeo* salts after their colors. The praseo salt possesses the trans configuration, and the violeo salt is the cis isomer. The configurations of these two isomers are shown in Fig. 5-5.

Corresponding to this form of isomerism are the two dinitrotetrammine salts of cobalt with the formula $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{X}$, where X is a halide anion. One of these salts is yellow-brown (the cis isomer), and the other one is yellow (the trans isomer).

The introduction of three univalent ions (acid radicals) into the

coordination sphere of a cobaltammine complex produces a nonionized compound. Thus, if three nitro groups are introduced into the coordination sphere of $[\text{Co}(\text{NH}_3)_6]^{3+}$, the resulting compound will be a nonelectrolyte with a formula of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$. On the basis of the octahedral theory this substance should exist in the form of two isomers. Experimentally, however, the configurations of the two isomers have not as yet been rigidly established. On the other hand it is of interest to note that only two isomers are possible for a complex with the general formula $[\text{Ma}_3\text{b}_3]$. The configurations of these isomers are given in Fig. 5-6.

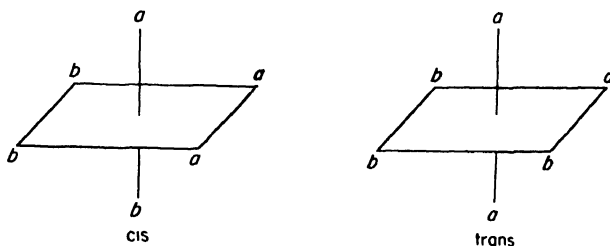


Fig. 5-6 The two isomeric forms of a complex with a general formula $[\text{Ma}_3\text{b}_3]$.

Again, there is one cis position and one trans position for coordinating groups of these numbers.

5-26 Optical Isomerism. The existence of mirror-image isomers is a consequence of the octahedral structure of complexes with a coordination number of 6. In fact the octahedral theory is confirmed by the occurrence of optically active isomers. *Optical isomerism* arises when two compounds exist which have configurations of atoms or groups in space about the central atom such that one structure is the mirror image of the other. This phenomenon is also called *enantiomorphism*. An optically active substance has the power of rotating the plane of polarized light transmitted through it. The plane of the ray may be rotated to the right, in which case the substance is called the dextrorotatory (*d*) form, or it may be rotated to the left, in which case the substance is designated as the levorotatory (*l*) form. On the other hand, if the ray of polarized light is not affected, the substance is termed inactive.

Optical isomerism occurs in octahedral structures of the type $[\text{M}(\text{AA})_3]$, in which AA represents a symmetrical bidentate group like ethylenediamine or the oxalate ion. Figure 5-7 gives the configurations for $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, which are mirror-image forms of compounds of this type. When compounds of this kind are synthesized, they appear as inactive mixtures of the two optically active isomers and the isomers must be separated by special methods. The inactive mixtures are usually termed *racemic mixtures*.

Optical isomerism also appears in complexes with the general formulas $[M(AA)_2b_2]$ and $[M(AA)_2ab]$. These types are of even greater interest because they exist in three forms: two optically active isomers and one inactive compound. Moreover mirror-image isomerism is possible only

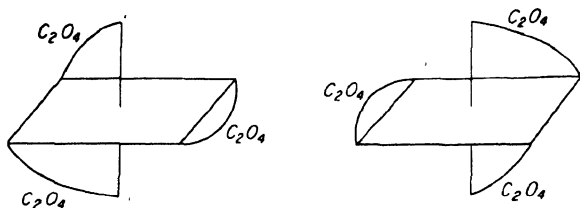


Fig. 5-7 Mirror-image forms of $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$.

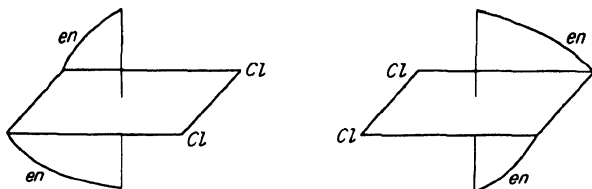


Fig. 5-8 Optically active isomers of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ with cis configurations.

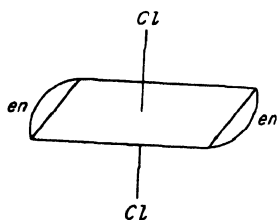
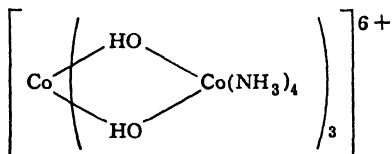


Fig. 5-9 Inactive isomer of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ with trans configuration.

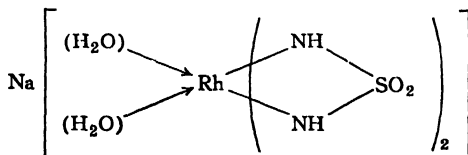
when the two nonchelate (unidentate) coordinating groups occur in a cis configuration. A compound rotates the plane of polarized light when it is possible to construct two molecular models which are mirror images of each other. Such models cannot be superimposed upon each other and are said to be *asymmetric*. The optically active isomers with cis configurations for $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ are shown in Fig. 5-8. On the other hand, when the unidentate groups are in the trans position, the complex has a plane of symmetry and is optically inactive. The configuration for $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ with the unidentate groups in the trans position is shown in Fig. 5-9. The "en" in Figs. 5-8 and 5-9 is an abbreviation for ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. This organic molecule forms a bidentate grouping because of its ability to attach itself at each end to the central atom.

The majority of chelate compounds are produced by the multiple attachments of organic molecules to central metal atoms (Sec. 5-14). Furthermore optical isomerism and the asymmetric carbon atom are among the cornerstones of structural organic chemistry. Consequently, at first it was thought that optical activity in coordination compounds

might be due to asymmetric carbon atoms within the organic molecules attached to the central atoms. Although Werner's theory predicted optical activity among octahedral complexes with bidentate groupings, it seemed desirable to confirm the octahedral theory by preparing optically active compounds of purely inorganic nature. Two such compounds have been prepared and resolved, one by Werner¹ in 1914, and the other by F. G. Mann² in 1933. The resolution effected by Werner was that of the hexol dodecammine tetracobaltic ion, which has the formula of



The resolution accomplished by Mann was with the sodium salt of diaquodisulfamidorrhodium, which has the formula



It is beyond the scope of this book to give an account of these investigations, but the preparation and resolution of optically active inorganic compounds gave brilliant confirmation to the Werner theory.

5.27 Stereoisomerism in Square-planar Complexes. Four coordinating groups may be placed about a central metal atom in two spatial arrangements. The central atom is placed either in the center of a tetrahedron with the coordinating groups on each corner or in the center of a square-planar structure with the four coordination positions occupying the corners of the quadrilateral. The two possibilities are indicated in Fig. 5-10. Although both spatial arrangements are found among the coordination compounds of the metals, isomerism occurs more frequently among compounds with a square-planar arrangement than among those with a tetrahedral structure. The reasons for this disparity of isomeric forms between the two possible structures will become apparent as our discussion continues.

No stereoisomers are possible with either the tetrahedral or the planar structures for those complexes of the types $[\text{Ma}_4]$, $[\text{Ma}_3\text{b}]$, and $[\text{Mab}_3]$, because all possible arrangements of components in each of these sub-

¹ A. Werner, *Ber., deut. Chem. Ges.* **47**: 3087 (1914).

² F. G. Mann, *J. Chem. Soc.*, 1933, p. 412.

stances are exactly the same. In the case of materials of the type $[Ma_2b_2]$, cis and trans isomers may be predicted for the planar structure, but none are possible for the tetrahedral. The cis and trans isomeric arrangements for the planar structure are given in Fig. 5-11. In these arrangements the cis isomer is designated as the one with similar groups in adjacent positions and the trans isomer as the one where these groups are opposite.

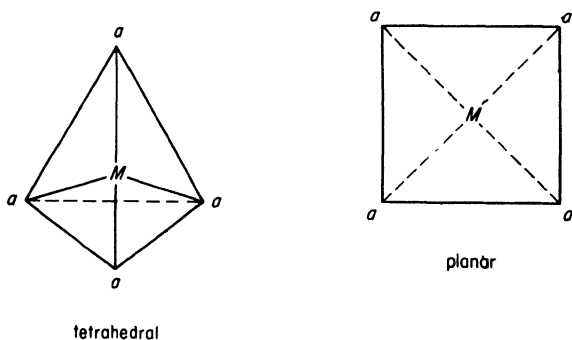


Fig. 5-10 Spatial arrangements for compounds of coordination number 4.

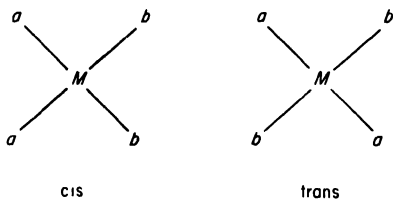


Fig. 5-11 The cis and trans isomeric arrangements for the planar structure of a compound of type $[Ma_2b_2]$.

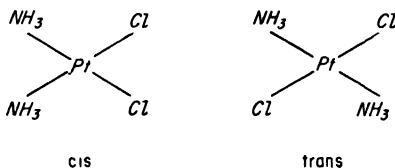
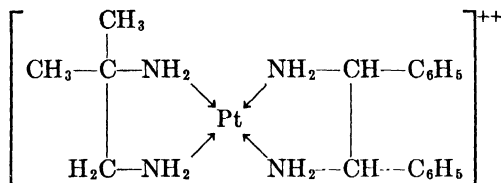


Fig. 5.12 The *cis* and *trans* isomers of diamminedichloroplatinum.

The existence of diamminedichloroplatinum in two isomeric forms led Werner in 1893 to propose a planar arrangement for the four valencies of the platinum atom. The spatial arrangements in these isomers are given in Fig. 5-12. Since that time dozens of such isomeric pairs have been studied, and proof of the planar structure for many tetravalent metals has been obtained by X-ray studies. Particularly is this true for compounds of nickel, palladium, and platinum. By means of X-ray analyses it has been proved that the anions $[\text{PtCl}_4]^-$ and $[\text{PdCl}_4]^-$ are planar and that the four nitrogen atoms in the cation $[\text{Pt}(\text{NH}_3)_4]^{++}$ are in the same plane as the platinum atom. Additional confirmation of the planar arrangement of the valency bonds of the platinum ion came from the discovery of three isomers for the cation $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{C}_6\text{H}_5\text{N})(\text{NO}_2)]^+$.

In addition to X-ray analysis other physical methods have been used to prove the correctness of the planar distribution. Janes¹ has measured the magnetic susceptibilities of the more important four-coordinated palladium compounds, and his results support certain planar arrangements. One of the most convincing methods of determining the structures of complex compounds is the measurement of dipole moments. Jensen² has demonstrated that, for a large number of platinum complexes of the type Ma_2b_2 , the dipole moments are large for cis isomers and zero for trans forms. The only possible explanation for this behavior is a planar configuration for bivalent platinum.

Probably the most unique proof of a planar distribution of the valencies about tetravalent platinum has been obtained by Mills and Quibell.³ Without going into a complete explanation of their ingenious method, it may be outlined briefly by saying that they succeeded in preparing an optically inactive mixture of stilbenediaminoisobutylenediamino platinumous salts and then resolved the tetraammine mixture into two stable optically active isomers. The general formula for the complex is



The construction of three-dimensional models of this structure reveals the fact that, if the platinum atom is tetrahedral, the complex possesses a plane of symmetry and therefore cannot be resolved into isomers. The fact that it is resolvable into stable enantiomorphs is elegant proof of the planar arrangement of the platinum valencies.

5-28 Stereoisomerism in Tetrahedral Complexes. The stereochemistry of carbon compounds indicates that in the tetrahedral arrangement it is possible to have isomerism only when all four coordinating groups are different. Thus in a compound of the type $[Mabcd]$, when the arrangement is tetrahedral, the attachment of four different atoms or groups should result in the production of a pair of enantiomorphs (mirror-image isomers). On the other hand, with this configuration, no other type of isomerism is possible. The mirror-image isomers of this type are indicated graphically in Fig. 5-13.

Although the tetrahedral configuration in molecules and ions such as

¹ R. B. Janes, *J. Am. Chem. Soc.*, **57**: 471 (1935).

² K. A. Jensen, *Z. anorg. Chem.*, **225**: 97 (1935).

³ W. H. Mills, and T. H. H. Quibell, *J. Chem. Soc.*, 1935, p. 839.

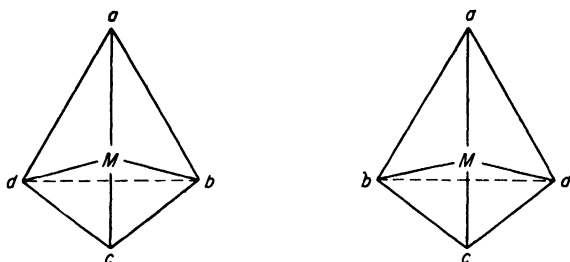
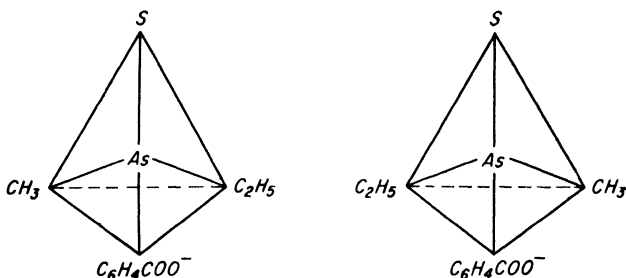
Fig. 5-13 Mirror-image isomers of a compound of type $[Mabcd]$.

Fig. 5-14 Optically active isomers of an arsenic compound with a tetrahedral structure.

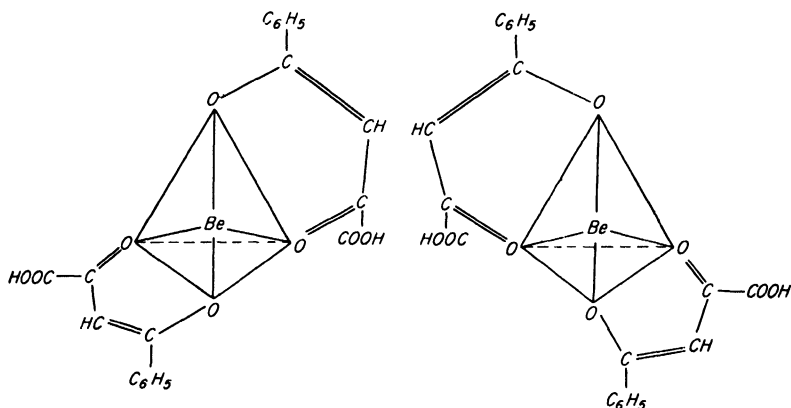


Fig. 5-15 The optically active isomers of beryllium benzoylpyruvate.

$(\text{NH}_3)_2\text{ZnCl}_2$, CoCl_4^- , and $[\text{Pt}(\text{CH}_3)_3\text{Cl}]$ is quite common, stereoisomerism is of fairly rare occurrence. It might be well to repeat that where stereoisomerism does exist in tetrahedral complexes it must necessarily be in the form of optical isomerism. Furthermore the synthesis and resolution of asymmetric molecules or ions have almost invariably involved the presence, in the complex, of substituted hydrocarbon groups or radicals. For

this reason such compounds are of interest and importance in the field of organic as well as that of inorganic chemistry. For example, an optically active arsenic ion with three organic groups attached is indicated in Fig. 5-14.

Asymmetry and optical activity in a tetrahedral configuration may be attained in chelate structures for certain types of compounds. The tetrahedral structure of beryllium chelates has been demonstrated by the separation of beryllium benzoylpyruvate into two optically active isomers. The diastereoisomeric forms are given in Fig. 5-15. It should be noted that the attachment of two identical by *nonsymmetrical* chelate groups confers the necessary asymmetry to the molecule.

EXERCISES

1. What is meant by the coordination number of a cation? Give two specific examples, and describe their probable structures.
2. How is the coordination number of a cation determined?
3. In the compound K_2PtCl_6 designate those ions which are in the inner sphere and those ions which are in the outer sphere of the central atom.
4. Explain how the charge on a complex ion is computed.
5. How does the Werner theory account for the different forms of the compound $CrCl_3 \cdot 6H_2O$?
6. Explain the formation of a coordination compound or a complex ion in terms of the electronic theory.
7. What, if any, is the difference between coordinate bonding and covalent bonding?
8. What elements are prone to form coordinate bonds? Why?
9. Which is more important in coordinate bonding, the tendency to fill incomplete stable orbitals, or the tendency to attain a symmetrical packing structure?
10. What is the relation between amphoteric hydroxides and complex hydroxide ions?
11. Describe the probable binding which occurs in the octahedral complex $Al(H_2O)_6^{3+}$.
12. Suggest a reason why HCl and not H_2O is liberated when $AlCl_3 \cdot 6H_2O$ is heated.
13. Why should the NH_3 molecule have a greater tendency to form an electron-pair bond than the water molecule?
14. Water molecules may be bonded to the central atom in coordination compounds either by coordinate bonds or by ion-dipole bonds. Explain.
15. Explain why the complex $Al(NH_3)_6^{3+}$ does not exist in aqueous solution.
16. Suggest reasons why certain aquo complexes produce decidedly acid solutions.
17. Why should $Al(H_2O)_6^{3+}$ be a stronger acid than $Mg(H_2O)_6^{++}$?
18. How may magnetic data serve to distinguish between ionic and covalent bonding in complex ions?

266 Fundamental Concepts of Inorganic Chemistry

19. List and describe the various factors which apparently affect the stability of a complex ion.

20. Compile a list of electron donors (molecules or ions) which may enter into complex formation.

21. What is a chelate compound? Give three examples of such compounds, and describe their structures.

22. Chelates may be classified according to the nature of the linkages they contain. Explain with examples for each type within the classification.

23. Suggest why a chelated complex is more stable than a complex which is similar but unchelated.

24. Explain the reasons for the increasing interest in, and the importance of, the field of chelate chemistry.

25. Explain, and illustrate with examples, what is meant by the term isomerism.

26. What is the difference between ionization isomerism and coordination isomerism?

27. Discuss the possibility of isomerism in the complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$.

28. How many structural isomers of the octahedral complex $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ are possible?

29. How many isomers are possible for the complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$?

30. Discuss the possibility of isomerism in the complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

31. How many isomers of the tetrahedral complex $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$ are possible?

32. Indicate possible configurations for the isomers of the planar, square complex $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

33. Is it possible for $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ to exhibit optical isomerism? Explain.

34. Draw diagrammatic representations of the isomers of $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$.

35. Give the possible configurations of the stereoisomers of the complex $[\text{Co}(\text{NO}_2)_3(\text{OH})_3]^{3-}$.

36. Optical activity among octahedral complexes with bidentate grouping is predicted by the Werner theory. Suggest reasons why only two such compounds, of purely inorganic nature, have been prepared.

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CHAPTER 6

Inorganic Reactions in Aqueous Solutions

It should be obvious that particles (ions, atoms, or molecules) of chemically active substances must be brought together before any type of reaction is possible. The most widely used medium for this purpose is water, which may play a multiple role in bringing about chemical reactions between particles. Moreover the reacting particles must be in a dispersed condition before appreciable interaction can take place. Consequently, before entering into a discussion of reactions in aqueous solution, our first task should be an attempt to explain the action of water as a dispersing medium.

THE PROBLEM OF SOLUBILITY

By definition a solution is a homogeneous mixture of two or more substances, these substances being of molecular dimensions, whose composition may be varied within certain limits. In other words, a solution may be regarded as a molecular dispersion of substances within each other. In aqueous solutions the water is usually considered as the solvent, or medium in which the solute is dissolved. There are, however, conditions where the two components of a simple solution, the solvent and solute, cannot be distinguished from each other, as illustrated by a mixture of water and ethyl alcohol. In a mixture of 75 per cent alcohol and 25 per cent water the alcohol might well be regarded as the solvent and water as the solute. Totally miscible combinations of this type are not common. Usually there is a limit to the solubility of a substance in water, and when this limit is reached, the undissolved solute exists in equilibrium with the dissolved solute, as a saturated solution.

In general the particles encountered in solutions of inorganic substances are derived from solids which have been dissolved in water. There are, however, other mixtures recognized as solutions. For example, gases, such as ammonia and carbon dioxide, or liquids, such as

hydrogen cyanide and hydrogen fluoride, can be dissolved in water to form solutions.

The range of solubility of solids in water is quite wide. Potassium nitrate dissolves to the extent of 31.6 g in 100 ml of water at 20°C, whereas silver chloride is soluble only to the extent of 0.0001 g/100 ml of water at 10°C. Why one substance is very soluble and another only slightly soluble may be explained in terms of the attractive forces between the solute particles and solvent molecules. A completely satisfactory analysis of these attractive forces is yet to be made, but sufficient basic facts about solubility are known to enable us to visualize a partial picture of what takes place when a solute dissolves in a solvent.

6.1 The Effect of Temperature on Solubility. A rising temperature produces a wide range of effects upon the solubilities of solids in water. Usually the solubilities of substances are increased with an increase in temperature, but there are exceptions to this general rule. Among these exceptions are anhydrous sodium sulfate, whose solubility decreases with rising temperature, and sodium chloride, whose solubility is little affected by temperature change. The solubility-temperature curves in Fig. 6.1 illustrate the different effects of temperature upon three different salts.

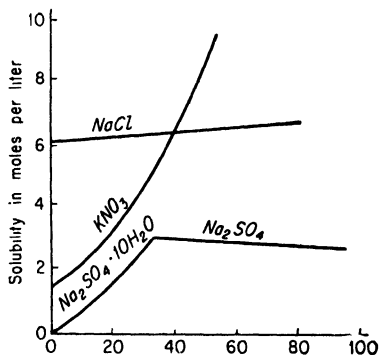


Fig. 6.1 Effect of temperature on the solubility of certain soluble salts.

The solution of a solid is analogous to a melting process. Pure solids are usually crystalline in structure, and the atoms or ions in the crystal lattice are geometrically interspaced so that each ion or atom has the same pattern with respect to neighboring ions or atoms (Sec. 4.9). The forces which hold these ions or atoms in their relative positions may be quite large. However, when a crystal is heated, the kinetic energy of the particles within the solid is increased. This increased energy is manifested, at first, by an increased vibration of the particles composing the lattice structure. When the amplitude of vibration becomes sufficiently large, the forces holding the particles together are overcome and the ions or atoms break away from their relatively fixed positions. In this manner a crystal melts, and the particles of which it was originally composed are free to move throughout the molten substance. In like fashion, when a solid enters into aqueous solution, the solvent particles exert sufficient attraction to overcome the attractive forces holding the solute particles in

the crystal lattice. As a general rule, a rise in temperature favors an increase in solubility. The electrostatic forces holding ions or molecules within a crystal are weakened by an increase in the kinetic energy of these particles, thereby enabling the attractive forces of the solvent molecules to be more effective in breaking down the crystal lattice. It is also true that substances with high melting points are more insoluble than those with low melting points. A high melting point indicates a greater intermolecular or interionic attraction. However, so many factors enter into the complicated picture of the solution process that the foregoing explanation is far from complete.

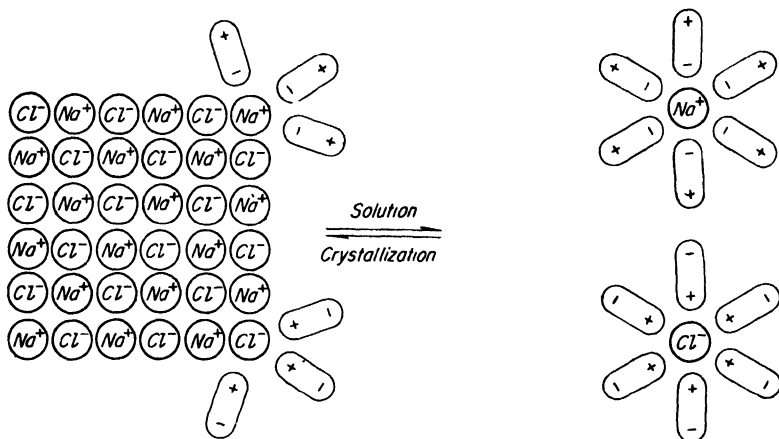


Fig. 6-2 Schematic diagram of the solution process of an ionic compound.

6-2 The Role of Water as a Solvent. The electrical dissymmetry of the water molecule is explained in Sec. 4-16, and a diagrammatic representation of the electronic structure of this molecule is given in Fig. 4-16. The displacement of electric charges within its structure accounts for the polar character of the particle. As a result of the separation of positive and negative charges the water molecule is oriented in an electrostatic field, in a manner similar to that of a small magnet in a magnetic-field. Furthermore the polarity of the H_2O particle enables it to exert an attractive force toward a charged body.

Ionic substances, such as sodium chloride, exist as ions, not only in solution, but also in the crystal. In the process by which a solid of this type enters solution, water molecules, because of their dipole moments, align their negative centers toward the positive ions and their positive ends in the direction of the negative ions at the surface of the crystal. The dipole forces exerted by the oriented water molecules weaken the interionic attraction within the crystal so that some of the ions are pulled

into solution. The removed ions wander away from the crystal and may carry their attached water molecules with them, although there is some doubt as to the advisability of distinguishing between solvent molecules which are attached to an ion and those which remain unattached. If it is assumed that six water molecules are attached to each ion, then a schematic diagram of the solution process may be indicated as in Fig. 6-2.

Ionic compounds are more soluble in solvents with high dielectric constants. This property, sometimes called *specific inductive capacity*, is a measure of the ability of a solvent to modify the mutual interaction of electrified bodies immersed in it, or separated by it. Those solvents which have large dielectric constants also have large separation of charges within their molecules. Consequently the magnitude of the dielectric constant of a solvent is also a measure of its polarity. Furthermore the degree of polarity depends upon the distance between charges within a molecule. Ordinarily, the degree of polarity is designated as the *dipole moment* of the molecule, and the dipole moment is calculated by multiplying the distance between the centers of the two charges by the magnitude of one of the charges. Thus

$$\mu = de$$

where μ denotes the dipole moment. Figure 6-3 indicates polar molecules with different polarities resulting from differences in the extent of the separation of the intramolecular charges. The dipole moment is always of the order of 10^{-18} esu. This magnitude is to be anticipated since the unit electronic charge is 4.8×10^{-10} esu and the diameter of most molecules is of the order of 10^{-8} cm. Table 6-1 lists a number of liquid compounds according to their decreasing dipole moments.



Fig. 6-3 Schematic representation of molecules with increasing degree of polarity.

TABLE 6-1 DIPOLE MOMENTS OF A NUMBER OF LIQUIDS

Liquid compound	Dipole moment, esu
$\text{C}_6\text{H}_5\text{NO}_2$ (nitrobenzene)	4.18×10^{-18}
H_2O (water)	1.84×10^{-18}
$\text{C}_2\text{H}_5\text{OH}$ (ethyl alcohol)	1.70×10^{-18}
$\text{C}_6\text{H}_5\text{OH}$ (phenol)	1.70×10^{-18}
NH_3 (liquid ammonia)	1.46×10^{-18}
CHCl_3 (chloroform)	1.15×10^{-18}
HBr (liquid hydrogen bromide)	0.79×10^{-18}
C_6H_6 (benzene)	0
CCl_4 (carbon tetrachloride)	0

The dipoles in water are attracted to each other by fairly strong forces called *hydrogen bonds*. Consequently, for a substance to be soluble in water, it must be capable of weakening the hydrogen bonding in order

that the solute particles may penetrate into the intermolecular spaces of the solvent. When water molecules are subjected to the electrostatic field of an ion, there is a tendency for the dipole to be aligned, or rotated, in the direction of the field. Any alignment, or rotation, results in a slight displacement of the oppositely charged parts of each molecule and a consequent loss of potential energy by the molecules of the solvent. In other words, the dipoles of water are attracted by the electrostatic charges of ions, resulting in a weakening of hydrogen bonding in the solvent and a penetration by the ion into the intermolecular spaces of the liquid. On the other hand bonding forces between polar molecules of water prevent the entrance of nonpolar molecules into the intermolecular spaces of the solvent. It might be said that nonpolar molecules do not enter into solution in a polar solvent because of a squeezing-out effect. Thus water dissolves an ionic solid, such as sodium chloride, but will not dissolve paraffin, which is a nonionic and a nonpolar solid. For similar reasons water dissolves ammonia, both substances being strongly polar, but will not dissolve a nonpolar gas such as methane.

6.3 Chemical Structure and Solubility. "Like dissolves like" is a familiar rule in organic chemistry and is also applicable to inorganic chemistry. This rule refers to similarity in relation not only to dipole moment but also to chemical composition. It is generally true that a substance tends to dissolve in a solvent which is chemically related in composition to the substance. For example, paraffin readily dissolves in gasoline, or water is good solvent of cane sugar. Gasoline and paraffin are both hydrocarbons—compounds containing only carbon and hydrogen. Cane sugar is a carbohydrate and, as the name "carbohydrate" implies, is a composition of carbon, hydrogen, and oxygen in which the ratio of hydrogen to oxygen is the same as in water.

The explanation of the process of solution becomes more complex when the solvent is a liquid whose molecules are associated as a result of hydrogen bonding. Among solvents of this type are water, liquid ammonia, and liquid hydrogen fluoride. The hydrogen bond is produced where the hydrogen atom serves as a bridge between two strongly electronegative atoms. Consequently molecules which contain hydrogen attached to the more electronegative atoms tend to group into clusters which are held together by hydrogen bridges. The tetrahedral arrangement of water molecules in ice is a result of hydrogen bonding, and this tetrahedral structure persists, to some extent, after ice is converted into a liquid. Therefore the composition of water is not that of simple H_2O molecules but that of multiple molecules held together somewhat loosely by hydrogen bonds. Water, liquid ammonia, liquid hydrogen fluoride, and solvents of this type, because of their associated structures, will not necessarily dissolve polar molecules unless the solute molecules can form

hydrogen bonds with the solvent molecules. For example, nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, has a dipole moment of 4.18×10^{-18} esu, which is large as compared with the dipole moment of water, but nitrobenzene molecules are practically insoluble in water because they cannot form hydrogen linkages with water molecules. On the other hand phenol, $\text{C}_6\text{H}_5\text{OH}$, is more than forty times as soluble in water as nitrobenzene. Phenol, which is similar to nitrobenzene in that it is a monosubstituted benzene product, has a dipole moment of 1.7×10^{-18} esu and should be less soluble than nitrobenzene if relative solubility were entirely dependent upon the magnitude of the dipole moment. This unexpected solubility must be due to the formation of hydrogen bonds between the hydroxyl groups of the phenol molecules and the oxygen atoms in the water molecules.

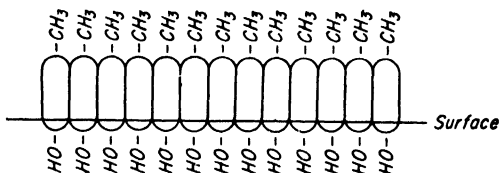


Fig. 6-4 Diagrammatic representation of the unimolecular film formed on an interface of water by long-chain organic molecules with polar end groups.

Another complex form of solubility is presented by organic molecules whose structures are such that they are partly polar and partly nonpolar. A molecule of this type is exemplified by heptyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, which is composed of a hydrocarbon chain with a hydroxyl group attached to one end. The hydroxyl end of this molecule is soluble, because it penetrates the structure of water to form hydrogen bonds with the solvent. The hydrocarbon end of the molecule is nonpolar and cannot form hydrogen bonds and is therefore insoluble in water. Molecules of heptyl alcohol, when placed in water, are pushed to the surface, where they orient themselves so that the soluble ends are in the water and the nonpolar ends protrude above the surface. Figure 6-4 illustrates this arrangement. It is of interest that hydrocarbon molecules with soluble polar end groups such as $-\text{CH}_2\text{OH}$ or $-\text{COOH}$ may form unimolecular (a depth of one molecule) films upon the surface of water. Films of this type also occur at any interface of water and its "wetting" properties may undergo decided changes. Wetting agents of this general type have wide commercial applications.

The size, charge, and electronic structure of each ion in the crystal lattice of an ionic compound affect the solubility of the particular electrolyte. Although certain generalizations regarding the influences of these factors are somewhat obvious, it is impossible to arrive at any hard and

fast rules concerning these structural variations. Large ions should pack less tightly in a lattice than small ions of similar charges, because of the greater distances between the effective charges borne by the larger particles. This observation is confirmed by an examination of Table 3-15. In this table the radii of the sodium and fluoride ions are listed as 0.95 and 1.36 Å, respectively, whereas the radii of the cesium and iodide ions are given as 1.69 and 2.16 Å. Consequently it may be assumed that the lattice energy of cesium iodide is less than that of sodium fluoride because of the differences in the radii of the ions which make up the two compounds. The values given for certain lattice energies in Table 4-3 verify the foregoing assumption. According to this table the lattice energy of sodium fluoride is 213.4 kcal, and that of cesium iodide is 139.1 kcal. Furthermore solubility data for the two compounds indicate that cesium iodide is approximately ten times as soluble in water as is sodium fluoride.

High ionic charges should decrease the solubility of an electrolyte. The effect of increased ionic charge upon solubility is illustrated by the compounds magnesium oxide and barium oxide. Since the ions in these two substances are doubly charged, the particles should pack more tightly in the crystal lattice than might be expected in the case of monovalent ions. The radii of the magnesium, barium, and oxygen ions are listed as 0.65, 1.35, and 1.40 Å, respectively, and these values would indicate that the ions of magnesium oxide should be held more firmly in its lattice than are the ions in barium oxide. Such a prediction turns out to be true, inasmuch as the lattice energy of magnesium oxide is given as 940 kcal as compared with a value of 747 kcal for barium oxide. A comparison of the solubilities of the two compounds shows that barium oxide is over 2,000 times more soluble than magnesium oxide.

From the examples given in the preceding paragraphs it might appear that the tightness with which ions are held in a crystal lattice should always involve the simple relationship of an attractive force operating between two charged bodies. In other words, one might conclude that the strength of the coulombic bond between two ions is always proportional to the product of the two charges and inversely proportional to the square of the distance between the effective centers of the two ions. Such a conclusion would be erroneous, as is indicated by the relative solubilities of magnesium sulfate and barium sulfate. The radii of the doubly charged magnesium, barium, and sulfate ions are 0.65, 1.35, and 3.0 Å, respectively, and from these values it might be wrongly deduced that both compounds are insoluble and that barium sulfate is more soluble than magnesium sulfate. Nevertheless it so happens that magnesium sulfate is quite soluble and barium sulfate is fairly insoluble. The explanation for this apparent anomaly lies in the large difference between the radii of the magnesium and sulfate ions. On the basis of coulombic

attraction alone, magnesium sulfate should be quite insoluble; however, the small magnesium ions cannot fill up the large spaces between the sulfate ions in the crystal lattice. In order to attain effective packing, each magnesium ion is surrounded by a number of water molecules in such wise that the resulting hydrated particle is sufficiently large to fill its allotted space in the lattice. As a result of this hydration the force operating between the hydrated magnesium ion and the sulfate ion is so weak that the ions are easily separated in producing an aqueous solution.

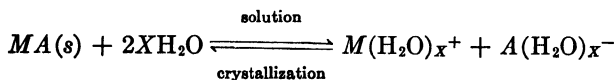
The relation between solubility and binding forces in a crystal lattice is far from simple. In a crystal produced by the deposition of ions there frequently appears a tendency for the electrovalencies of the constituent particles to acquire a covalent character. This tendency is designated as *polarization* and usually depends upon the extent to which the anion may be deformed and upon the polarizing power of the cation (Fajans' rules, Sec. 4.5). In other words, a small positive ion may distort a large negative ion, and in the process an electron may be pulled away from the anion to form an electron pair or covalent linkage. The effect of polarization may be illustrated by the structures of the silver halides. The crystals of AgF, AgCl, and AgBr have a sodium chloride crystal structure, but as the anion in these compounds increases in size, the polarizing effect of the small Ag^+ ion becomes stronger. In fact the bonding in AgI has very little ionic character, and the crystal has a structure that is characteristic of certain covalent compounds, usually designated as the zinc blende, ZnS, structure. Spectroscopic data indicate that silver iodide is composed of atoms and not of ions.

6.4 Solubility Resulting from Chemical Reaction. The difference between a physical solution and a chemical solution offers no sharp line of demarcation. A physical solution is one in which the solute and solvent are both nonpolar, with no associating tendencies or solvating propensities. A solution of paraffin in benzene is a typical example of a physical solution. On the other hand the solubility of calcium oxalate in dilute hydrochloric acid is the result of a chemical reaction, and such a solution is clearly a chemical solution. Between the two extremes of physical and chemical solubilities are solutions formed by attractive forces which are intermediate between physical and chemical. The solubility of sugars in water can be attributed to the formation of hydrogen bonds. The solubility of most ionic compounds in water results from the solvation of ions to form hydrated ions. Yet neither the solubility of sugars nor the solubility of ionic compounds is caused by either physical forces or chemical forces alone. It is more likely that such intermediate types of solubility are a result of a combination of chemical and physical forces.

As a general rule salts dissolve more readily in solvents composed of molecules containing electrostatic dipoles. In the solid state an ionic

compound exists as ions which are arranged in a symmetrical fashion within the crystal lattice. The nature of the packing, or arrangement, of ions in the lattice is determined largely by the diameters of the ions. Furthermore the ions are held in their relative positions by strongly electrostatic forces resulting from the charges upon the ions. To break down the architecture of the crystal, these electrostatic forces must be overcome. As was described in Sec. 6.1, the solution of a solid is analogous to a melting process. The amount of energy necessary to cause the solution of a gram-formula weight of solid sodium chloride should be equivalent to the amount of energy required to melt an equal weight of the same compound. In the process of bringing an electrolyte into solution it is generally assumed that there is an interaction between the polar molecules of water and the ions of the crystal, in which the dipoles of the water molecules are oriented, or aligned, in such a fashion as to exert a pulling force to overcome the attractive forces between the ions within the crystal. For a substance to be readily soluble, more energy must be available to break down the crystal than was liberated in building up the ionic lattice (Sec. 4.6). In other words, the energy of solvation must be of greater magnitude than the lattice energy. Moreover energy of solvation may come from two sources: the dipole attraction of solvent molecules for ions in the crystal, and the chemical reaction between the ions and the water molecules to form hydrated ions with a resulting liberation of energy. Since these two sources of energy are not easily distinguishable, it is more convenient to consider them collectively as the energy of solvation. Then, it may be said that the solubility of a salt is proportional to the magnitude of, and difference between, two energy factors: the lattice energy and the energy of solvation.

Electrolytes in which the lattice energies of the crystals are relatively large are usually not very soluble in water. The reaction of a solid electrolyte with water may be indicated by the equation

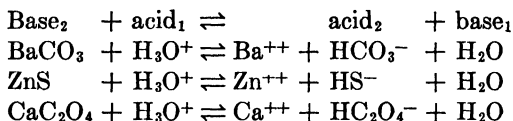


The extent to which the solid will dissolve depends upon the amount of energy necessary to pull the two ions away from the crystal and the total energy released by the hydration of the ions. The energy required for the separation of solid ions into gaseous ions is the lattice energy of an ionic compound (Sec. 4.6) and may be calculated by the Born-Haber cycle (Sec. 4.7). The energy produced in the reaction is from the hydration of the gaseous ions. Unless the solvation energy is greater than the lattice energy, the electrolyte will not be appreciably soluble. Both

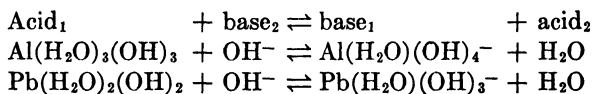
energy factors are dependent upon the size, charge, and electronic structure of each ion involved in the reaction. The effects of these structural variations upon solubility have been discussed in the preceding section.

The process by which a solute enters into solution by reaction with a solvent is called *solvolysis*. When water is the solvent, the solvation is accomplished by an interaction to produce hydrated ions. Whether this interaction can be classified as a chemical reaction is debatable. Certainly it will depend to some extent upon whether the ions entering solution have definite water molecules bonded to them. It is now believed that for most ions one cannot properly distinguish between those solvent molecules which are attached to an ion and those which remain unattached. In contrast to the interaction between a lattice ion and the solvent that bathes it there are other types of reactions that bring solid materials into solution which may be unquestionably classified as chemical. Most of these reactions are either acid-base reactions or those involving oxidation and reduction.

Certain ionic and some covalent compounds may act as proton donors or proton acceptors and in acid-base reactions may be converted from insoluble substances to soluble ions or molecules. By way of illustration, many insoluble carbonates, sulfides, oxides, and oxalates may act as bases in reacting with hydronium ions to produce soluble products. A more detailed explanation of acid-base reactions is given in another division of this chapter. It suffices to say that, according to the Brønsted definitions of acids and bases, an acid is a proton donor and a base is a proton acceptor. Also, according to the Brønsted interpretation the reaction of an acid and base produces another acid and base; therefore any acid-base reaction involves two acids and bases. Equations for reactions of this type are given as follows:



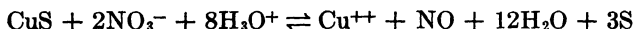
A few insoluble hydrated hydroxides may act as acids in reacting with hydroxide ions in aqueous solutions. Examples of such acid-base reactions are



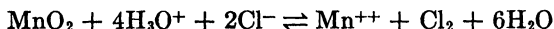
Various insoluble solids may be rendered soluble by the action of oxidizing or reducing agents in aqueous solution. Inasmuch as the topic of

278 Fundamental Concepts of Inorganic Chemistry

oxidation and reduction makes up a separate division in this chapter, we shall not attempt any explanation of this type of reaction but shall be content with two simple examples. The first of these examples is the oxidizing action of nitric acid in bringing cupric sulfide into solution, as given in the equation



The second example illustrates the reducing action of hydrochloric acid in dissolving manganese dioxide, according to the equation



ACID-BASE SYSTEMS

The nature of acids and bases has been a matter of speculation since the time of Robert Boyle in the seventeenth century. Even today the problem of explaining the fundamental actions of these substances has provoked many avenues of approach. This statement does not necessarily imply that the various interpretations of acid-base systems are conflicting or controversial, but simply that each interpretation involves different implications. Moreover it cannot be said that any one of the several concepts of acid-base systems is better than the others. Each theory possesses certain distinctive merits that appear most applicable for the system for which it was conceived.

6.5 Historical. The word *acid* comes from the Latin word *acidus*, meaning *sour*, since a sour taste was one of the early characteristic properties recognized in this class of substances. Other distinctive properties were first described by Boyle, who stated that acids had a high solvent power, the ability to change certain vegetable dyes from one color to another, and the capacity of precipitating sulfur from its solutions in alkalies. The first descriptive term for a substance opposite in properties to an acid was *alkali*, a word derived from the Arabic words *al-qili*, meaning the *ashes* of a plant. Besides certain powers which we now recognize as detergent properties, the chief characteristic first established for an alkali was its ability to destroy the action of an acid. Later the term *base* was applied to certain nonalkaline substances, as, for example, heavy metal oxides, which would react with acids but did not possess typical alkaline properties. In 1774 Rouelle extended the notion of what constituted a base by defining it as any substances which reacts with an acid to form a salt.

The first important *theory* concerning acidity was advanced by Lavoisier, who in 1787 postulated that acids were binary compounds containing oxygen. His experiments showed that a number of elements, as, for example, carbon, nitrogen, and sulfur, burned in oxygen to give com-

pounds which acted as acids in water solution. This acid-oxygen theory gained many adherents, and almost a generation elapsed before it was recognized that acids do not necessarily contain oxygen. Although Berthollet in 1787 offered experimental evidence that certain acids contain no oxygen, it was not until 1810 that Davy produced convincing proof that hydrochloric acid contained no oxygen. In 1814 he wrote "that acidity does not depend upon any particular elementary substance, but upon peculiar arrangement of various substances." Yet it soon became evident that Davy's concept of an acid was also inaccurate and that acids do contain an elementary substance, which is hydrogen. Thus the early hydrogen theory of acids may be stated in effect as: All acids contain hydrogen, but all hydrogen compounds are not acids. Additional support to the hydrogen theory was advanced by Liebig, who in 1838 defined acids as "compounds containing hydrogen, in which the hydrogen can be replaced by metals." This definition was accepted with little modification for a period of nearly 50 years.

6-6 The Water-Ion System. In 1887 a young Swedish chemist Svante Arrhenius, after working on the conductance of acid solutions for his doctor's thesis at the University of Stockholm, advanced the theory of ionization to account for the properties of aqueous solutions of electrolytes. This theory revolutionized the thinking in inorganic chemistry and inspired extensive research in the field of solutions. It also offered the first modern approach to the acid-base concept. Although the classical theory of Arrhenius has been modified by more recent theories and discoveries, it is still applicable with little change to the behavior of acids and bases in aqueous solution.

According to the Arrhenius theory *an acid is defined as a hydrogen compound which in water solution gives hydrogen ions, and a base is a hydroxide compound which in aqueous solution yields hydroxide ions.* The process of neutralization results from the union of hydrogen ions with hydroxide ions to form water molecules.

The Arrhenius interpretation of the nature of acids and bases is subject to a number of objections. Among various possible criticisms may be listed the following:

1. The theory defines acids and bases in terms of aqueous solutions, and not in terms of the substances themselves. Consequently the substance HCl is regarded as an acid only when dissolved in water, whereas in other solvents, such as benzene, or in the gaseous state it is not considered as an acid.

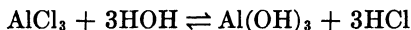
2. The Arrhenius interpretation places emphasis upon hydrogen ions in aqueous solution. It offers no explanation for the acid properties of a salt such as NH_4NO_3 in a liquid ammonia system where no hydrogen ions are present.

3. An artificial explanation is necessary in this concept to explain the basicity of an aqueous solution of ammonia. Thus, according to the Arrhenius theory, ammonia must react with water to produce ammonium hydroxide, which in turn ionizes to produce hydroxide ions according to the equations



There is no proof for the existence of the compound designated as ammonium hydroxide, and the assumption of such an ionization is entirely misleading.

4. The Arrhenius theory offers no satisfactory explanation for the acidity of certain salts such as aluminum chloride. The assumption that a salt of this type may hydrolyze in the following manner,

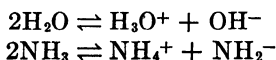


is worse than misleading—it is totally untrue.

5. Another objection to the hydrogen-ion concept of acids is the improbable idea of a bare proton existing in an aqueous solution. The hydration energy of the hydrogen ion has been calculated as 256 kcal/mole; consequently it is to be expected that this ion can exist only in the hydrated form.

In spite of the many serious objections to the Arrhenius theory of acids and bases it is unrivaled in its simplicity. In first-year chemistry water is indicated as the solvent for almost all reactions in solution, and the Arrhenius concept of acids and bases is quite adequate for an elementary approach.

6.7 The Solvent System. The concept of the solvent system as a means for explaining acid-base behavior had its origin with E. C. Franklin¹ in 1905. Extending the Arrhenius idea of acids and bases in aqueous solution to liquid ammonia, Franklin reasoned that if water ionizes into hydronium and hydroxide ions liquid ammonia should ionize in a similar fashion into ammonium and amide ions. The equations for the two analogous ionization reactions may be indicated as



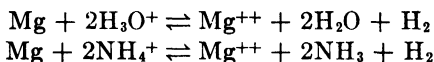
It is common knowledge that the addition of hydronium ions in the form of a strong acid to a water solution increases the hydronium-ion concentration and lowers the hydroxide-ion concentration of the water equilibrium. Conversely the addition of hydroxide ions shifts the water equilibrium in the opposite direction. In like manner, the addition of ammonium ions in the form of an ammonium salt to liquid ammonia

¹ E. C. Franklin, *J. Am. Chem. Soc.*, **27**: 820 (1905).

shifts the ammonia equilibrium to increase the ammonium-ion and decrease the amide-ion concentration. Also, the addition of amide compounds produces an opposite effect upon the latter equilibrium. Therefore, just as the hydronium ion is an acid and the hydroxide ion is a base in aqueous solutions, so may the ammonium ion act as an acid and the amide ion as a base in liquid ammonia solutions. Furthermore the ammonium and amide ions may be titrated against each other in liquid ammonia, using phenolphthalein as an indicator, in the same fashion as more familiar titrations are made between acids and bases in aqueous solutions. The neutralization equation can be written as



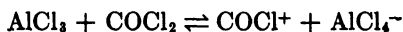
The similarity between chemical reactions in liquid ammonia and water may be demonstrated by many other types of equations. A more detailed discussion of these reactions is given in Chap. 7; however, the behavior of acid solutions of these solvents toward metals is pertinent to our present discussion. The fact that certain metals will cause the evolution of hydrogen when reacting with either hydronium ions in water or ammonium ions in ammonia indicates that the acid properties of both the hydronium and the ammonium ions are due to the proton which each contains. In other words, the hydronium ion is a hydrated proton, and the ammonium ion is an ammoniated proton, both ions behaving as acids. Moreover there is more justification for the formula NH_4^+ than there is for that of H_3O^+ . Typical equations for the reactions of a metal with acid solutions of the two solvents are



The solvent-system theory of acids and bases has been extended to include systems which are nonprötonic in nature. For example, anhydrous aluminum chloride dissolves in phosgene to increase the conductivity of the solvent one hundred thousandfold. To explain this increased conductivity, it has been suggested that the concentration of ions in the solvent has been increased as a result of the reaction of aluminum chloride with the solvent to produce a complex ion. It has been assumed that pure phosgene is ionized to a very slight extent, as indicated by the equation

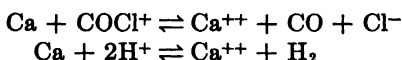


Furthermore it is believed that the concentration of cations is increased when the solvent reacts with aluminum chloride, and a possible equation for such a reaction is



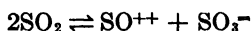
282 Fundamental Concepts of Inorganic Chemistry

The preceding reactions are of unusual interest inasmuch as the resulting solution of aluminum chloride in phosgene will dissolve metals with the evolution of carbon monoxide. Moreover the same solution may be neutralized by metallic chlorides such as calcium chloride. In other words, the solution reacts in a manner similar to an acid although *no protons* are involved in the acidic reaction. By way of illustration, calcium reacts with the phosgene solution to liberate carbon monoxide in a reaction which is analogous to the action of the same metal with water. The equations for the two reactions may be indicated as

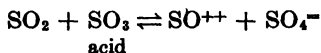


With the addition of aluminum chloride the concentration of solvent cations in phosgene has been increased so that the reaction of the solution with a metal is much more rapid than that of the solvent alone. Consequently aluminum chloride may be defined as an acid because when dissolved in phosgene it causes the solvent to act as an acid. In terms of the foregoing discussion *an acid may be defined as a solute which imparts a cation characteristic to the solvent, and a base as a solute which gives rise to an anion characteristic in the solvent.* The process of neutralization, in terms of the solvent system, is the union of the solvent cation with the solvent anion to produce the solvent.

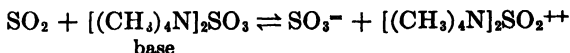
Reactions similar to those just given have been observed in other solvents. Among these the behavior of liquid sulfur dioxide as a solvent for acid-base solutes may be considered as typical. The slight ionization of pure liquid sulfur dioxide probably produces thionyl and sulfite ions according to the equation



Among those solutes which increase the cation concentration of the solvent is sulfur trioxide; hence this solute may be considered as an acid. The equation for increased cation activity is

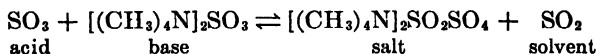


The most effective bases in liquid sulfur dioxide are sulfites of organic amines, among which tetramethylammonium sulfite may be considered as typical. A possible reaction for increased anion activity in liquid SO_2 , with this solute, may be indicated as



The union of the *acid* solute and the *base* solute produces a *salt* solute and may be regarded as part of the process of neutralization. A possible

equation for the reaction in liquid sulfur dioxide is

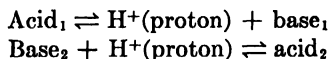


Amphoteric reactions similar to those of aluminum and zinc hydroxides in aqueous solution also occur in other solvents according to the theory of solvent systems. Reactions of this type are discussed in Chap. 7.

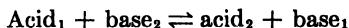
The explanation of acid-base behavior by means of the solvent system extends the concepts and definitions for acids and bases to include solutions in which the solutes are not proton donors. This broader viewpoint has the advantage of explaining acidic behavior in nonaqueous and non-protonic solutions. It has the serious disadvantages of limiting acid-base phenomena to solvent systems and overemphasizing the importance of ionization on acid-base properties. Certainly there is ample experimental evidence of certain neutralizations occurring without the presence of ions, and any acid-base theory which does not account for such reactions is necessarily limited in its scope. Furthermore it would seem that any satisfactory extended theory should be able to explain those acid-base reactions which may occur in the absence of a solvent, which the *solvent-system* theory does not. Therefore it may be concluded that the solvent system for acids and bases simply extends, but does not necessarily improve, the Arrhenius water-ion system.

6-8 The Proton-Donor-Acceptor System. In an attempt to overcome some of the limitations of the Arrhenius concept of acid-base behavior a more general definition for acids and bases was proposed almost simultaneously in 1923 by J. N. Brønsted¹ in Denmark, and T. M. Lowry² in England. According to this definition *an acid is a substance having a tendency to lose one or more protons, and a base is a substance having a tendency to add protons*. Since Brønsted has done much more than Lowry to develop this approach, it is generally designated as the *Brønsted theory*.

In the terms of the Brønsted-Lowry theory for acid-base phenomena the reaction of an acid with a base produces another acid and base. The fundamental relationship between an acid and a base is indicated by the following three equations:



and the sum of these two equations is



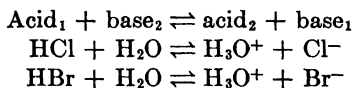
Therefore any acid-base reaction involves two acids and two bases, and these acids and bases are called *conjugate pairs*. In the preceding equa-

¹ J. N. Brønsted, *Rec. trav. chim.*, **42**: 718 (1923).

² T. M. Lowry, *Chemistry & Industry*, **42**: 43 (1923).

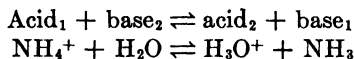
284 Fundamental Concepts of Inorganic Chemistry

tion the conjugate acid and base are designated by the same subscript; consequently acid₁ and base₁ form a conjugate pair, and base₂ and acid₂ are likewise a conjugate pair. To illustrate with specific examples, the compounds hydrogen chloride and hydrogen bromide in the liquid state are poor conductors of electricity and may be considered as covalent compounds, but in water solutions these compounds are strong electrolytes. Each of these substances is an acid, since each produces protons in water solution, and the water molecule can be considered to be a base, inasmuch as water molecules accept protons to form hydronium ions. In the first of the following equations the Cl⁻ ion is the conjugate base of the acid HCl; and the H₃O⁺ ion is the conjugate acid of the base, the water molecule.



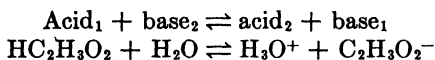
These two reactions illustrate the fact that certain covalent compounds may become strong electrolytes by solvation and the reactions with water are acid-base reactions.

Ions may also act as acids; e.g., the ammonium ion is an acid in aqueous solution. The equation for the reaction in this case is

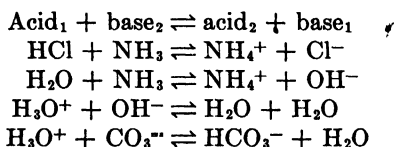


However, the ammonium ion is a weak acid since comparatively few hydronium ions are produced in this reaction.

Acetic acid is another weak acid producing few hydronium ions in solution. The acetic acid molecule is a covalent compound which reacts with the base, water, to a slight extent according to the following equation:



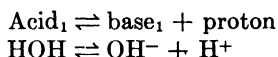
In the foregoing illustrative equations the base which accepted protons was the molecule, water; however, from the original definition, any ion or molecule which accepts protons is a base, as indicated in the following equations:



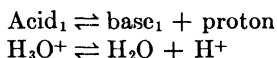
According to the Brønsted theory all negative ions, anions, are classified as bases, since they combine with protons. Those anions which form slightly dissociated substances with protons are considered as strong

bases, and those which form weak linkages with protons are weak bases. Thus, in aqueous solution, the hydroxide ion is the strongest base, and the chloride ion is one of the weakest; the acetate ion is a fairly strong base, whereas the nitrate ion is a very weak base. Strength of a base is measured by its ability to capture protons in competition with other bases.

In Table 6-2 are a number of acids and their conjugate bases. The acids are arranged in the order of decreasing strength, whereas the conjugate bases are naturally in the order of increasing strength. In other words, the strongest acids are those nearest the top of the first column, and the strongest bases are those occurring nearest the bottom of the second column. In this table water appears listed as an acid and also as a conjugate base. When water functions as an acid, its conjugate base is the hydroxyl ion,



When water functions as a base, its conjugate acid is the hydronium ion,



It may be observed that the pK for H_2O as an acid is approximately 16, and the pK for H_2O as a base will be the same value; consequently water is not only a very weak acid but also a very weak base. Any substance such as water which may function as either an acid or a base is designated by the term *amphiprotic*.

The Brønsted-Lowry interpretation of acid-base phenomena is a much broader concept than the one presented by the Arrhenius theory. It defines acids and bases in terms of the substances themselves, and not in terms of their ionization in aqueous solution. Moreover the idea of hydrolysis is not necessary to explain the acid character of NH_4^+ or the basic character of CO_3^{2-} . In terms of Brønsted definitions the basic character of NH_3 is indicated by the ability of this molecule to accept protons in forming the acid NH_4^+ . This is a wider viewpoint than that of the Arrhenius theory, in which a base is defined as a substance that produces hydroxide ions. Basic properties are indicated by the ability of a substance to capture protons. Furthermore the Brønsted approach recognizes that acid-base behavior is neither restricted to, nor dependent upon, any particular solvent.

Despite the fact that the Brønsted definitions possess certain advantages over those of Arrhenius, the former is still handicapped by the undue emphasis placed upon protonic exchange. One writer¹ aptly

¹ N. F. Hall, "Acids and Bases," p. 6, *Journal of Chemical Education*, Easton, Pa., 1941.

designates this theory as "the cult of the proton." Although the majority of acid-base reactions are characterized by the transference of protons, there are many reactions with acid-base characteristics in which no protons are involved (Sec. 6·7). The Brønsted definitions cannot satisfactorily account for these nonprotonic reactions.

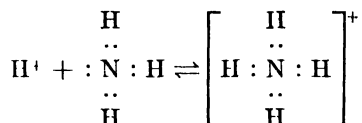
TABLE 6·2 THE RELATIVE STRENGTHS OF SOME ACIDS IN WATER SOLUTIONS

Acid	Conjugate base	Ionization constant	pK
HClO ₄	ClO ₄ ⁻		
HCl	Cl ⁻		
HNO ₃	NO ₃ ⁻		
H ₂ SO ₄	HSO ₄ ⁻		
H ₃ O ⁺	H ₂ O	55.5	-1.74
HIO ₃	IO ₃ ⁻	1.67 × 10 ⁻¹	0.78
H ₂ C ₂ O ₄	HC ₂ O ₄ ⁻	6.5 × 10 ⁻²	1.19
H ₂ SO ₃	HSO ₃ ⁻	1.72 × 10 ⁻²	1.76
H ₃ PO ₃	H ₂ PO ₃ ⁻	1.6 × 10 ⁻²	1.80
HSO ₄ ⁻	SO ₄ ⁻	1.2 × 10 ⁻²	1.92
H ₃ PO ₄	H ₂ PO ₄ ⁻	7.5 × 10 ⁻³	2.12
Fe(H ₂ O) ₆ ³⁺	Fe(H ₂ O) ₅ (OH) ²⁺	6.0 × 10 ⁻³	2.22
H ₃ AsO ₄	H ₂ AsO ₄ ⁻	5.0 × 10 ⁻³	2.30
HF	F ⁻	7.2 × 10 ⁻⁴	3.14
HNO ₂	NO ₂ ⁻	4 × 10 ⁻⁴	3.40
Cr(H ₂ O) ₆ ³⁺	Cr(H ₂ O) ₅ (OH) ²⁺	1.5 × 10 ⁻⁴	3.82
HC ₂ H ₃ O ₂	C ₂ H ₃ O ₂ ⁻	1.75 × 10 ⁻⁵	4.76
Al(H ₂ O) ₆ ³⁺	Al(H ₂ O) ₅ (OH) ²⁺	1.4 × 10 ⁻⁵	4.85
H ₂ CO ₃	HCO ₃ ⁻	4.3 × 10 ⁻⁷	6.37
HSO ₃ ⁻	SO ₃ ⁻	6.24 × 10 ⁻⁸	7.20
H ₂ PO ₄ ⁻	HPO ₄ ⁻	6.2 × 10 ⁻⁸	7.21
H ₂ S	HS ⁻	5.7 × 10 ⁻⁸	7.24
HOCl	OCl ⁻	3.5 × 10 ⁻⁸	7.46
HCN	CN ⁻	7.2 × 10 ⁻¹⁰	9.14
HAsO ₂	AsO ₂ ⁻	6.0 × 10 ⁻¹⁰	9.22
H ₂ BO ₃	H ₂ BO ₃ ⁻	5.8 × 10 ⁻¹⁰	9.24
NH ₄ ⁺	NH ₃	5.5 × 10 ⁻¹⁰	9.26
HCO ₃ ⁻	CO ₃ ⁻	5.6 × 10 ⁻¹¹	10.25
HPO ₄ ⁻	PO ₄ ³⁻	4.8 × 10 ⁻¹³	12.32
HS ⁻	S ⁻	1.2 × 10 ⁻¹⁵	14.92
HOH	OH ⁻	1.78 × 10 ⁻¹⁶	15.75
OH ⁻	O ⁻		

6·9 The Electron-Donor-Acceptor System. In 1923 G. N. Lewis proposed a new concept of acids and bases founded upon the electronic theory of valence. It was the same year that the joint proposals of Brønsted and Lowry appeared. However, Lewis did little to elaborate on his theory until 1938; consequently it was largely ignored until the later date. This theory is broader than the other views of acids and bases which have been described in that it explained the acid-base phenomena not in

terms of ionic reactions but in terms of bond formation. According to the Lewis interpretation of acids and bases a *base* is any substance that has a pair of electrons which it can donate to establish a coordinate bond, and an *acid* is any substance which may accept an electron pair to form such a bond. Therefore acids may be considered as being identical with Sidgwick's electron-pair acceptors and bases with his electron-pair donors (Sec. 5-3). Thus the process of neutralization is simply the formation of a coordinate bond between the electron-donor and the electron-acceptor particles.

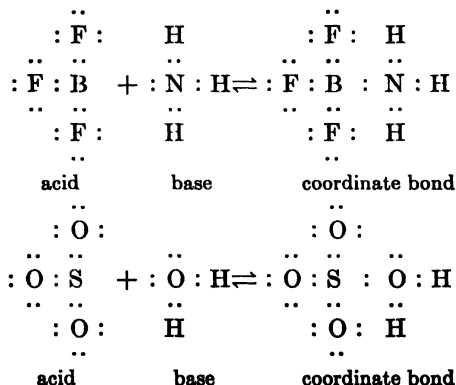
The Lewis classification of bases includes the same substances as the Brønsted-Lowry definition, since any molecule or ion which accepts protons does so because of the presence of an unshared pair of electrons. To illustrate this point, in the reaction between a proton and the ammonia molecule,



the latter is a proton acceptor according to the Brønsted definition and an electron-pair donor in terms of the Lewis explanation. Therefore, as far as bases are concerned, the two theories are identical except in the wording of the definitions.

The broadness of the Lewis theory becomes apparent in examining those substances which are classified as acids. For convenience in our discussion these substances may be divided into three types:

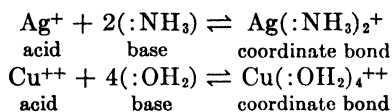
1. The first type of Lewis acids includes those molecules having less than a full octet of electrons. Typical examples of this class are boron trifluoride and sulfur trioxide, and the reactions between these compounds and typical bases are given in the following equations:



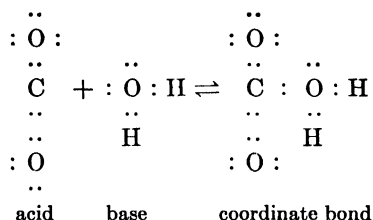
288 Fundamental Concepts of Inorganic Chemistry

Again it is pointed out that the process of neutralization is the formation of a coordinate bond.

2. The second class of Lewis acids is made up of those positive heavy metal ions with incomplete stable orbitals, as, for example, the silver and copper ions. The reactions of these ions with bases are identical with those reactions which produce Werner complexes (Secs. 5·2 and 5·3). This is to be expected since neutralization, according to the Lewis theory, produces coordinate bonds. Typical examples of reactions for these positive ions are indicated in the following equations:



3. A third type of Lewis acids is composed of molecules containing double bonds, excepting those with the C=C bonds. One such molecule is carbon dioxide, and its reaction with water is a typical acid-base reaction. The electronic interpretation of this interaction is given in the following equation:



The Lewis concept of acids and bases may be considered as an improvement over previous views inasmuch as it recognizes that the transfer of protons is only a particular form of acid-base behavior. As a result of a broader interpretation it includes those reactions with acid-base characteristics in which no protons are involved. In this respect the Lewis theory is superior to the Brønsted-Lowry definitions.

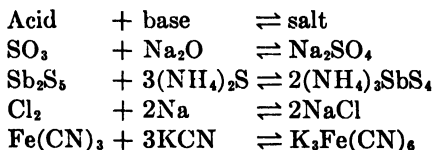
The electron-donor-acceptor theory suffers from at least two disadvantages. First of all, the Lewis acids differ in relative strengths depending upon the base with which they react; consequently it is not possible to arrange them in any order of strength relative to each other. Second, the concept is so broad that it is unsuited to general chemistry, in which the explanation of acid-base behavior is most important. To some extent the interpretation of acid-base phenomena is analogous to the classification of the elements. The best system may be so complex as to be totally unsuited to the instruction of beginners. Beyond the

beginning course a student should have learned enough chemistry so that any system can be properly evaluated without instruction.

6-10 The Positive-Negative System. The most fundamental concept of acids and bases has been offered by M. Usanovich of the Central Asiatic University at Tashkent. According to his theory an acid is any substance that produces cations, combines with anions, or forms salts with bases in the course of neutralization. In other words, an acid is a cation, a cation donor, an electron-pair acceptor, or an oxidant. In a similar fashion a base is defined as any material that is capable of either giving up anions or electrons or combining with cations. Not only does this interpretation include all acid-base phenomena which have been described in the other theories, but it also considers oxidation-reduction processes to be a special form of acid-base behavior.

In explaining the origin of acid-base behavior in molecules, Usanovich accounts for such action in terms of polar valence. In general the acidic or basic property of a molecule is dependent upon the valence of the atoms of which it is composed, and usually the effect of the atom of highest valence is most pronounced. This explanation goes back to some earlier observations relating to the periodic functions of the elements. It will be recalled (Sec. 3-20) that the acidic character of the elements increases in progressing from left to right in the Mendeleev table of the elements. Therefore the oxides of the alkali and alkaline earths are essentially basic in nature, whereas the oxides of nitrogen and sulfur are predominantly acidic. Likewise the basic nature of the elements increases in passing from the top to the bottom of the periodic table; consequently it is to be expected that a molecule such as As_2O_3 is more acidic than one composed of related elements lower in the table, for example, Sb_2S_3 . According to this theory the higher valence of an element produces a more acidic molecule than a lower valence: hence SnS_2 is more acidic than SnS . Usanovich also emphasizes the importance of what he terms "coordination unsaturation," by which he means the ability of an atom to increase its covalence. To him the acid function within a molecule depends upon the presence of a coordinately unsaturated positive atom and the basic function upon the presence of a negative atom similarly unsaturated.

Examples of neutralization in terms of the Usanovich concept are given in the following equations:



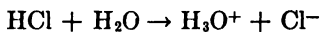
Although the Usanovich theory is broader than that of Lewis, it does

not require that a student be familiar with the electronic structure of the reacting particles and, to this extent, it is simpler and easier to present to beginning students. After all, the criterion of any acid-base theory will rest upon its suitability as a teaching device in elementary chemistry. The great disadvantage of the Usanovich viewpoint is its extreme generality. A student in elementary chemistry would most certainly have difficulty in recognizing whether certain substances are acids or bases, especially in the absence of identifying equations. Furthermore the inclusion of oxidation-reduction reactions as acid-base phenomena is open to question. Such reactions might better be considered on the basis of oxidation-reduction alone.

6-11 The Strengths of Acids. Five different interpretations, or systems, of acids and bases have been presented. As we have said in our introduction to this topic, it is impossible to designate any one of these concepts as being better than the others. Each theory has distinctive merits which may be more applicable for some particular purpose. Moreover, in attempting to define or compare strengths of acids, the problem again arises as to what constitutes an acid and under what conditions such a substance may be compared with similar compounds.

Acids may be divided into protonic and nonprotonic compounds, and the solvents in which they are dissolved may be likewise classified. According to the Lewis theory those substances which are experimentally classified as acids are electron acceptors and may be nonprotonic in nature. Inasmuch as neutralization, according to this concept, amounts to the formation of a coordinate bond, protons may, or may not, be involved in the reaction. Also, the strength of an acid as an electron acceptor depends not only upon the electronic configuration of the acid but also upon the base with which it reacts and the solvent in which the reaction takes place: Very little quantitative work has been done with Lewis acids, and it is doubtful that any simple relative values can be established for them.

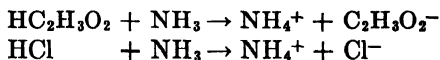
The apparent strength of a protonic acid is dependent upon the solvent in which the acid is dissolved. In water solutions the difference in strengths between acids such as hydrogen perchlorate, hydrogen chloride, hydrogen bromide, and hydrogen nitrate is obscured because these compounds react completely with the solvent in dilute solutions. The reaction between hydrogen chloride and water,



goes almost completely to the right because the water molecule is a much stronger base than is the chloride ion. Similar reactions take place for the other acids, just named, when placed in water solution. In all cases the acid which is left in solution is the hydronium ion, and the original

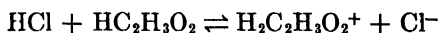
acids appear to be equally strong. This phenomenon is known as the *leveling effect* of the solvent.

Solvents more basic than water produce a leveling effect on a larger group of acids. Thus, in liquid ammonia, acetic acid is apparently as strong an acid as are hydrochloric or nitric acids, since ammonia has leveled the strength of these acids so that they appear to be 100 per cent ionized. The ionization reactions of hydrogen acetate and hydrogen chloride in liquid ammonia may be indicated as



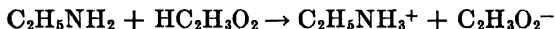
The ammonia molecule is a much stronger base than either the acetate or the chloride ion and displaces these ions from their hydrogen compounds.

A solvent more acidic than water has a smaller leveling effect. This statement may be illustrated by a comparison of the strength of hydrogen chloride when dissolved in water and when dissolved in acetic acid. In water solution the reaction between hydrogen chloride and water molecules goes practically to completion. However, the same solute dissolved in acetic acid produces only a slight reaction. The reaction may be indicated as



Apparently acetic acid is a weak base, as is the chloride ion, and there is little tendency for the reaction to proceed to the right. In this same solvent other protonic acids react in varying degrees. Consequently it is possible to compare certain of the so-called "strong" acids. Experimental results indicate that, with acetic acid as the solvent, the relative strengths of certain hydrogen acids are in the following order: $\text{HClO}_4 > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$.

A solvent more acidic than water has a pronounced leveling effect upon the strengths of bases. All bases which are stronger than aniline in water appear to be completely ionized in acetic acid solution. Thus all amines appear to be strong bases in this solvent, and a typical ionic reaction of this kind may be illustrated by the one between ethylamine and acetic acid,



It seems plausible that the reaction proceeds almost completely to the right because the amine is a much stronger base than is the acetate ion and displaces this ion from its hydrogen compound.

To obtain true evaluations of acid strengths, it is necessary to use non-protonic (aprotic) solvents. Solvents of this type are benzene, ether, and chloroform. Relatively little research has been performed along this line, but some data do exist for these particular solvents. The aprotic

nature of a solvent such as benzene renders it inert in the presence of acids and bases. Moreover, since there is no ionization reaction with the solvent, any comparison of acid strengths must be made in the presence of a base, and it is obvious that the reactants must be soluble in the stipulated solvent. An excellent discussion of these reactions is given by N. F. Hall.¹

6.12 Strengths of Acids in Aqueous Solutions. Since water is the solvent that is commonly used for acid-base reactions, it is pertinent to examine those factors which appear to affect the strength of acids in aqueous solutions. To facilitate our discussion we shall divide acids into three groups: (1) the *hydro* acids, such as HCl, in which the proton is attached directly to the central atom of the molecule; (2) the *oxy* acids, as illustrated by H₂SO₃, in which the proton is attached to an oxygen atom, the latter being bonded to the central atom; and (3) the hydrated cation acids, as exemplified by Al(H₂O)₆³⁺, in which the proton is released from a water molecule bonded to the central ion. Other acids are known in which the proton is bonded to a negative element, other than oxygen, which is in turn attached to the central atom, as for example, H₂PtCl₆. However, we shall confine our attention to the three groups of acids that have been enumerated.

For those hydro acids derived from the elements of any given periodic family the strengths of the acids increase with increasing molecular weight. The elements of Groups VIB and VIIB of the Mendeleev table may be used to illustrate this progressive change in strength. When the acids derived from these two series are arranged in the order of their increasing acidities, they appear as

	H ₂ O	H ₂ S	H ₂ Se	H ₂ Te	(strongest acid is H ₂ Te)
and	HF	HCl	HBr	HI	(strongest acid is HI)

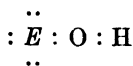
This order in acidity is the reverse of the ionic character in the compounds of the particular series. The strongest acid possesses the least ionic character. Thus H₂Te is the strongest acid in its series but also the least ionic of the four acids. However, these opposite properties are not contradictory, inasmuch as acid strength is measured by the ease with which a proton may be removed and ionic character is dependent upon the electronegativity (size and nuclear charge) of an element. In other words, it is easier to remove a proton from a large ion than a small one. It will be recalled that Coulomb's law relating to electrostatic forces states that the force attracting two charged bodies is directly dependent upon the magnitude of the two charges and inversely proportional to the square of the distance separating them. Therefore the fact that HI is a strong acid and HF is a weak acid may be attributed to the interatomic

¹ N. F. Hall, *Chem. Revs.*, **8**: 191 (1931).

distances between the ions of the two compounds. In HF the interatomic distance has been estimated as 1.0 Å, and in HI the distance is 1.7 Å.

In moving horizontally across the periodic table the strengths of acids, derived from elements in this progression, increase as the electronegativities of the elements increase. The series $\text{H}_3\text{N}-\text{H}_2\text{O}-\text{HF}$ illustrates an increase in acidity with electronegativity. In these elements the change in ionic size (Table 3-15) is relatively small as compared with the increase in ionic character of the bond formed with hydrogen.

For oxygen acids the strength of a particular acid is determined by the electronegativity and size of the central atom. Of these two factors the former is of greater influence upon the acidity of the compound. As previously stated, an oxy acid is one in which the proton is attached to an oxygen atom, the latter being bonded to the central atom. Therefore the general structure of such an acid may be designated as



in which E symbolizes the central element. In a hypothetical acid of this type the size and electronegativity of E determine the extent to which the electron pair, shared with the oxygen atom, is displaced from an intermediate position toward the central atom. If E is a small, strongly electronegative element, the electron pair shared with oxygen will be pulled away from the oxygen atom and this displacement will in turn cause a shifting of the electron pair between oxygen and hydrogen toward the oxygen atom. In other words, a highly electronegative element will cause a shifting of both electron pairs toward the central atom. The net effect is a weakening of the bond between the hydrogen and oxygen atoms, resulting in a compound from which a proton may split off readily. On the other hand, if the central atom is large and sufficiently electropositive, the two electron pairs will be displaced toward hydrogen, causing a weakening of the bond between oxygen and the central element. Under these conditions the hydroxide ion tends to split off, and the compound from which it is derived may be designated as a base.

The foregoing discussion may become more meaningful if illustrated with concrete examples. In the case of two oxy acids of similar structure, such as H_2SO_3 and H_2SeO_3 , the one containing the more electronegative central atom (in this instance, H_2SO_3) is the stronger. On the other hand, if we compare two dissimilar compounds, for example, ClOH and NaOH , we find that the central atom in the first example is electronegative, whereas in the second it is definitely electropositive. Consequently, as might be expected, HClO is classified as an acid and NaOH as a base.

294 Fundamental Concepts of Inorganic Chemistry

As a general rule the greater the number of negative atoms present in an oxy acid, the stronger is the acid. The truth of this generality is illustrated by the oxy acids of chlorine, HClO — HClO_2 — HClO_3 — HClO_4 , in which the acid strength increases greatly with each additional oxygen atom.

In the case of hydrated cation acids the strength of a given acid is determined by the size of the central ion and the magnitude of its charge (Sec. 5.5 and Table 5.4). Consequently the hydrated ferric ion is a fairly acidic complex since the ferric ion is small and bears a high charge. It is believed that protons split from coordinated water molecules because of a displacement of electrons toward the central atom, resulting in a weakening of the O—H bond. The Brønsted type of reaction by which protons are produced is illustrated by the following equation:



Large cations with small charges such as cesium, rubidium, and potassium are either loosely hydrated or not hydrated at all and have little or no effect upon the pH of their solutions. Other ions of intermediate sizes and charges, such as strontium and calcium, are definitely hydrated (Sec. 5.4) and have weakly acidic properties in aqueous solutions.

REDOX SYSTEMS

It would be much simpler to avoid the topic of redox systems altogether. The implications involved in this topic are far-reaching, extensive, and sometimes ambiguous. Any complete discussion of these implications would provide sufficient material for another volume and is obviously beyond the scope of this book. On the other hand, to omit this topic completely is out of the question since oxidation and reduction reactions are among the most important reactions occurring in chemistry. We shall, however, confine our attention largely to an analysis of those oxidation-reduction relationships involved in the reactions of inorganic materials in aqueous solutions.

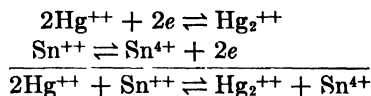
6.13 Definitions of Oxidation and Reduction. The term *oxidation* was originally used to designate a process by which substances acquired oxygen in chemical reactions and *reduction* for a process in which oxygen was removed from its compounds. In a restricted sense these meanings still hold true, but we now use these terms to include many reactions in which oxygen plays no part.

A broader concept of oxidation and reduction describes these processes in terms of *electron gain* and *electron loss*. Accordingly oxidation has been defined as a loss of one or more electrons by an atom, ion, or molecule; and reduction as the reverse process, in which electrons are added to a

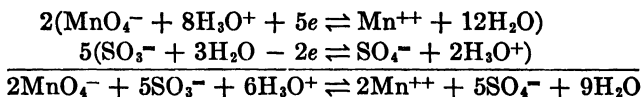
substance. More broadly a chemical reaction resulting in a change in the electric charges on the reacting particles may be called a *reduction-oxidation reaction*, or *redox* for short. The substance which furnishes the electrons is oxidized, and the substance receiving electrons is reduced. Consequently those substances which donate electrons easily are called *reducing agents*, and those which accept electrons readily are termed *oxidizing agents*. The two processes, oxidation and reduction, cannot take place separately but must occur simultaneously.

6.14 Half-reactions. Reactions which involve the donation or acceptance of electrons are called *electrode reactions* or *electron reactions*. Such reactions can take place either at electrodes, which supply and remove electrons, or by direct contact of atoms, ions, or molecules, if the contact produces an exchange of electrons.

The majority of oxidation-reduction interactions which take place in aqueous solution are ionic in nature. The net over-all reaction can frequently be written as the sum of two half-reactions. The equation for one half-reaction will indicate the release of electrons by one reactant, and the other half-reaction will show the capture of electrons by another reactant. For example, the reaction between stannous ions and mercuric ions may be indicated by equations as the sum of two half-reactions.



The use of half-reactions is convenient for balancing oxidation-reduction reactions. In writing the partial reactions in ionic form, care must be taken to balance not only the kind and number of atoms but also the sum of the ionic charges on both sides of the equations. Any unbalance of charge must be compensated by writing in free electrons. This method is known as the *ion-electron* method and may be illustrated by those equations involved in the reaction for the oxidation of the sulfite ion by the permanganate ion in an acid solution. The over-all equation for the complete reaction may be indicated as the sum of two actual electrode reactions.



From these reactions one may deduce that the permanganate ion acts as an oxidizing agent to accept electrons from the sulfite ion, which is a reducing agent under these conditions. The transfer of electrons from the reducing half-reaction to the oxidizing half-reaction is clearly indi-

cated, but no assumptions or speculations are necessary as to the mechanisms of the electron exchange.

6.15 Oxidation State and Oxidation Number. In ionic compounds composed of simple ions the oxidation state of an element is the same as the charge on the ion formed from an atom of the element. Thus, when sodium reacts with chlorine to produce sodium chloride, the oxidation state, or number, of the sodium is $+1$ and that of the chlorine is -1 . In some respects oxidation number is similar to valence, but whereas valence is a specific term defining the combining power of an element, the oxidation number is an obscure term designating an electric charge arbitrarily assigned to an atom, in either the free or the combined state. The use of such hypothetical electric charges has little or no theoretical justification, but they are convenient for balancing all types of redox equations.

The reactions between sodium and chlorine to produce ionic sodium chloride may be clearly described in terms of previous oxidation-reduction definitions. Sodium loses an electron and is oxidized, while chlorine gains an electron and is reduced in the same reaction. Not all redox reactions are so straightforward. In many such reactions it is difficult to determine which atoms lose and which gain electrons. For example, when hydrogen reacts with chlorine to form hydrogen chloride, there is no electron transfer, inasmuch as the resulting molecule is covalent. It might be argued that hydrogen chloride is a polar compound and, because of an unequal distribution of electrons, is the product of an oxidation-reduction reaction. The inadequacy of this reasoning is apparent by considering another familiar reaction of the same general type—the combustion of carbon to carbon dioxide. In the complete oxidation of carbon the product, carbon dioxide, is not only covalent but also a non-polar molecule.

To broaden the meaning of oxidation and reduction, and to include under this designation certain phenomena involving no electron transfer, it is convenient to introduce the concept of *oxidation number*. The oxidation number of an element in a compound or ion may be defined as the charge which an atom of the element would bear if the substance contained only ions.

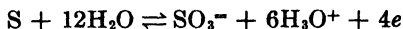
Oxidation numbers are usually assigned according to certain conventions. Atoms in an elementary state have an oxidation number of zero. Hydrogen has an oxidation number of $+1$ except in elemental hydrogen and hydrides. Oxygen is assigned an oxidation number of -2 except in elemental oxygen, peroxides, and the fluorine oxides. The algebraic sum of the oxidation states of all atoms in a compound must equal zero. The oxidation number of an element in a compound of uncertain structure may be calculated by assigning oxidation numbers to the other elements in the compound.

Oxidation numbers may also be evaluated by writing balanced equa-

tions for partial reactions involving the atom in question. Equations of this type are illustrated as follows:



The oxidation number of the sulfur atom in the sulfide ion S^{2-} is -2 since two electrons are gained in producing this ion from elementary sulfur. On the other hand, if electrons are lost in a partial reaction involving sulfur, as

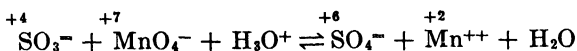


the oxidation number of the sulfur atom is positive. In the sulfite ion the oxidation number of sulfur is $+4$ since four electrons are released in forming the ion. The partial reaction by which the permanganate ion is formed from manganese indicates that seven electrons are lost in the process,

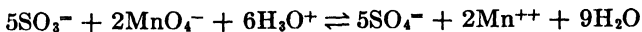


Consequently the oxidation number of the manganese atom in the permanganate ion is $+7$.

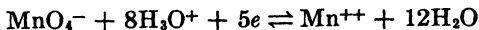
The use of oxidation states in balancing oxidation-reduction equations is known as the *oxidation-number method*. In this method oxidation is an algebraic increase in the oxidation number of an element, and, conversely, reduction may be defined as a decrease in the oxidation number of an element. The oxidation-number method may be illustrated by applying it to the same equation that was used for an example in the ion-electron method, i.e., the oxidation of the sulfite ion by the permanganate ion in an acid solution. The unbalanced equation showing oxidation-number changes is as follows:



In the reaction each manganese atom *apparently* gains five electrons, and each sulfur atom loses two electrons. The balanced equation contains five sulfur atoms, two manganese ions, and six hydronium ions.



The concept of oxidation numbers goes beyond the half-reaction explanation of electron transfer by implying that the electron exchange involves specific atoms within the reacting substances. In the half-reaction for the permanganate ion as an oxidizing agent,

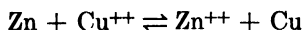


we are concerned not with the mechanism but with the fact that five electrons are acquired by the permanganate ion in its conversion to the manganous ion. On the other hand the oxidation-number method

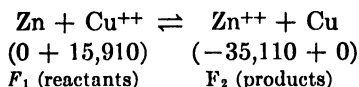
implies the presence of certain unrealistic charge distributions within reacting particles. The existence of the species Mn^{+7} or other species such as S^{+4} and S^{+6} is highly improbable. However, this criticism does not detract from the usefulness of oxidation numbers in the balancing of certain types of oxidation-reduction reactions.

6-16 The Driving Force of a Chemical Reaction. All chemical reactions involve changes in energy relationships. In 1879 Berthelot arrived at the false conclusion that the evolution of heat in a chemical reaction was a measure of the driving force of the reaction. However, the fact that many reactions proceed with the absorption of heat proves that Berthelot's idea could not be correct. A true measure of the driving force of a chemical reaction is the maximum work that can be obtained from the reaction under specified conditions. Substances combine chemically when their total energy contents change from a higher level of availability to a lower level. The change in total energy content is known as free energy. Thus, if the free energy of the reactants is greater than that of the products, the reaction will proceed. The size of the free-energy decrease is a quantitative measure of the driving force of the reaction. *Free energy* is defined as the capacity of a reaction for doing work, and it is a measure of maximum available work which can be obtained from a reaction regardless of whether work is done or not.

At the present time there is no method known for the determination of absolute values for free energies of various substances. On the other hand changes in free energy can be measured, and from such measurements it is possible to assign to a reacting substance a *relative* energy quantity called its free energy. To illustrate these statements, consider the reaction between zinc atoms and copper ions from which zinc ions and copper atoms are produced,



The absolute free energies of the substances involved in the reaction are not known, but, from their many familiar reactions, relative values, called *standard free energies*, have been assigned to them. The standard free energies of the Cu^{++} and Zn^{++} ions are 15,910 and $-35,110$ cal/gram atom, respectively; the free energies of the metals are taken as zero. From these values the change in free energy for the reaction between zinc atoms and copper ions may be calculated.



$$\begin{aligned} \text{Change in free energy} &= F_2 - F_1 \\ &= -35,110 - 15,910 = -51,020 \end{aligned}$$

Inasmuch as change in free energy measures the tendency of a reaction to proceed, there are three possibilities for any given chemical reaction:

1. If the free-energy change is a negative value, the reaction is spontaneous and will proceed in the direction in which the equation is written.
2. If the free-energy change is a positive value, the reaction is not spontaneous in the direction of the written equation but will proceed in the reverse direction.
3. If the free-energy change is equal to zero, the system is in equilibrium and the reaction will not proceed in either direction.

The reaction between zinc atoms and copper ions to produce zinc ions and copper atoms takes place from left to right, as written above, because there is a driving force, produced by a change in free energy, equal to $-51,020$ cal. Since the free-energy change of a chemical reaction is a quantitative measure of chemical affinity, such measurements are used by industrial as well as theoretical chemists to predict which chemical reactions can be expected to take place and which ones will not.

6.17 Oxidation Potentials. The driving force of an oxidation-reduction reaction may be measured not only in calories but also in terms of volts. The tendency of a substance to lose electrons may be designated as its *electrode potential*, or its *oxidation potential*. Where this tendency is measured under certain specified conditions, the resulting measurements are described as *standard electrode potentials*. It is customary to indicate the loss of electrons in the form of half-reactions; hence the tendency of a particular half-reaction to occur may be designated as its oxidation potential. In Table 6.4 are tabulated the oxidation potentials of a large number of half-reactions. The use of these data will be considered in Secs. 6.21 to 6.23.

The relation between standard oxidation potential and change in free energy may be represented mathematically as

$$\text{Change in free energy} = -nFE^0$$

where change in free energy is expressed in joules ($1 \text{ cal} = 4.183 \text{ joules}$), n is the number of electrons per atom or ion exchanged in the reaction, $F = 1$ faraday ($96,494$ coulombs), and $E^0 =$ volts (standard oxidation potential). Using this expression to determine the voltage produced by the reaction of zinc with a $1 F$ solution of cupric ions at 25°C , the equation becomes

$$4.183 \times 51,020 = 2 \times 96,494 \times E^0$$

$$E^0 = \frac{51,020 \times 4.183}{2 \times 96,494} = 1.10 \text{ volts}$$

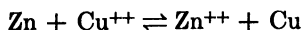
Therefore under these conditions the driving force of the reaction of zinc atoms with cupric ions to produce zinc ions and copper atoms is 1.10 volts.

6-18 Galvanic Cells. The driving force of a chemical reaction may be evaluated if the reaction can be arranged in the form of a galvanic cell from which the maximum electromotive force (emf) can be determined. Since emf results from a flow of electrons, such a reaction must necessarily be one involving oxidation and reduction. A galvanic cell is composed of electrodes dipping into solutions of electrolytes with electrical contact between electrodes and electrolytic contact between the solutions. The electrodes and solutions are so selected that a spontaneous chemical reaction takes place, resulting in an exchange of electrons.

A galvanic cell may be arranged by placing a solution of an oxidizing agent in one vessel and a solution of a reducing agent in another vessel. A conducting electrode is immersed in each solution, and electrolytic contact between the two solutions is established by means of a salt bridge. The latter is an inverted U tube containing a solution of an electrolyte. A flow of electrons is produced when external contact between the two electrodes is completed through a conducting wire. A simple galvanic cell may be constructed using a zinc electrode bathed by zinc ions in one vessel and a copper electrode immersed in a solution of cupric ions in another container. In this particular cell, electrons move along the wire from the zinc electrode to the copper electrode, since zinc loses its electrons more easily than does copper. The two half-reactions are



and the over-all reaction for the cell is expressed in the equation



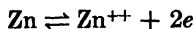
If a sensitive voltmeter is inserted in the external circuit, the voltage of the cell, when the reactants are at standard state (Sec. 6-20), is found to be 1.10 volts.

The cell cannot operate without a transfer of ions. As the zinc electrode goes into solution, the concentration of Zn^{++} becomes greater, whereas the deposition of copper at the other electrode decreases the concentration of Cu^{++} in the second solution. Consequently an excess of sulfate ions accumulates around the copper electrode and an excess of zinc ions around the zinc electrode. In any ionic solution the sum of the negative charges must equal the total positive charges. Hence, if no provision is made for the migration of ions from one vessel to the other, the current will cease to flow. The salt bridge provides a pathway for the transfer of ions between the two solutions so that the ionic charges within the solutions remain balanced.

It was stated that the potential difference between the zinc and copper electrodes is measured as 1.10 volts, but this potential is obtained only under certain specified conditions. Actually the magnitude of the

potential difference between the electrodes in an electrochemical cell depends upon many factors. Most important of these factors is the nature of the substances which make up the two half-cells. In other words, the driving force of the over-all reaction will depend upon the oxidation potentials of the two half-reactions. The simplest type of galvanic cell is one in which the electrodes are metals which enter into the chemical reaction. The tendency of a metal to lose electrons and go into solution as ions is called its *electrolytic solution pressure*. This tendency varies from metal to metal. If nickel were used in the reducing half-cell, replacing zinc, the potential of the cell would be lowered because nickel has a lower electrolytic solution pressure than zinc. On the other hand, if the copper-cupric-ion half-cell were replaced by the silver-silver-ion half-cell, the potential of the cell would be increased.

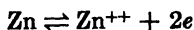
The concentration, or activity, of the ions of the metal in solution affects the potential of the electrode. In the case of the zinc-zinc-ion half-cell the concentration of the zinc ion is usually arbitrarily fixed at a given value to obtain the standard electrode potential. The half-reaction may be indicated as



If the concentration of zinc ions is increased, the equilibrium is shifted to the left, and from the principle of Le Châtelier it can be predicted that the charge on the electrode will be decreased. Therefore, when the half-cell is in operation with another half-cell, such as the copper-cupric ion, the increase in zinc ions and decrease in cupric ions will cause a decrease in potential produced. As the cell reaction proceeds, the cell "runs down" until, at equilibrium, the potential is zero.

Other factors of lesser importance which affect the potential difference between two half-cells are temperature and the emf arising at the liquid-liquid junction of the two half-cells, the latter being known as the *liquid-junction potential*. It is customary to describe electrode reactions as taking place at a constant temperature, arbitrarily selected as 25°C. Also, the salt bridge usually contains an electrolyte so chosen that the liquid-junction potential is reduced to a negligible quantity.

6-19 Single Electrode Potential. When a strip of metal, e.g., zinc, is placed in a 1 *F* solution of its ions, an equilibrium reaction develops between the metal and its ions as



The equilibrium expression may be written as

$$K_e = \frac{[\text{Zn}^{++}][e]^2}{[\text{Zn}]}$$

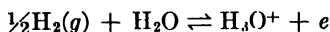
302 Fundamental Concepts of Inorganic Chemistry

The term $[Zn]$ may be omitted since the concentration, or activity, of a solid is constant for a given temperature; therefore

$$K_e = [Zn^{++}][e]^2$$

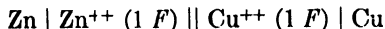
No method is known for determining the absolute value of the equilibrium constant for a half-cell reaction. Furthermore it is impossible to measure directly the electrode potential between a metal and a solution of its ions. Only the potential of a cell, resulting from a combination of two electrodes, may be determined experimentally.

To measure and evaluate potential differences between various half-cells, or potentials developed by various half-reactions, it is necessary to designate arbitrarily a particular electrode (or half-reaction) as a standard. The electrode which has been chosen for this purpose is the standard hydrogen electrode. This electrode is so constructed that hydrogen atoms are in contact with a 1 F (or activity equal to 1) solution of hydronium ions. Hydrogen gas, at 1 atm pressure and at a temperature of 25°C, is bubbled over a platinized platinum electrode which is immersed in a solution of hydronium ions. The finely divided platinum adsorbs hydrogen gas, which exists in equilibrium with hydronium ions, resulting in a definite electrode potential. The equation for the half-cell reaction is



This potential is arbitrarily assigned a value of zero.

6-20 Electrochemical Conventions. Certain conventions and notations have become fairly well standardized in connection with electrochemical cells. A half-cell, such as a strip of zinc immersed in a solution of 1 F Zn^{++} , is indicated as $Zn | Zn^{++} (1 F)$. The vertical line denotes a solid phase in contact with a liquid phase. The galvanic cell described in Sec. 6-18 may be designated as



where the liquid junction is represented by two vertical lines.

Many different types of electrodes, or half-cells, are possible. Some of these possibilities are given in Table 6-3, as well as the symbols designating examples of such electrodes.

TABLE 6-3 TYPES OF ELECTRODES

Metal, metal ion	$Zn Zn^{++}$
Inert electrode, nonmetal, nonmetal ion	$Pt Br_2(l) Br^-$
Inert electrode, metal ions in different valences.	$Pt Sn^{++}, Sn^{+}$
Inert electrode, gas, ion	$Pt H_2 H_3O^+$
Metal, insoluble salt, ion	$Ag AgCl Ag^+$

For purposes of comparison and reference, electrode potentials must be

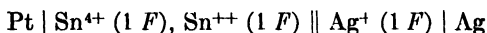
evaluated at a fixed temperature and under standardized conditions of concentrations. Thus Table 6-4 is a list of standard electrode potentials at 25°C in which the reactants are at unit activity. The term *activity* refers to effective concentration. In order to express activities numerically, it is customary to choose for each component of an electrode a reference state, known as the *standard state*. The activity is taken as unity in the standard state of a substance, and the actual standard state for a component is arbitrarily chosen as a matter of convenience.

The following standard states are generally accepted:

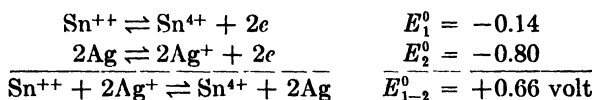
1. A gas is at standard state and unit activity at a pressure of 1 atm. When it is not at unit activity, the partial pressure, in atmospheres, is the effective concentration.
2. The standard state and unit activity of a liquid or solid are taken as the pure substance under atmospheric pressure.
3. The standard state of a solute in aqueous solutions is approximately 1 *F* (strictly, when $a = 1$).
4. The standard state and unit activity of a difficultly soluble salt are those of a saturated solution.

Potentials of half-cells, in which the reactants are at standard state, are represented as E^0 . The potential difference developed by two half-cells at standard state is indicated as $E_{1-2}^0 = E_1^0 - E_2^0$. Potentials of half-cells in which the reactants are not at standard state are denoted by the symbol E .

The voltage of a cell is the algebraic difference of the potentials of the two half-cells.¹ For example, consider the cell



By convention, the half-cell reaction of the right-hand electrode is subtracted from the half-cell reaction of the left-hand electrode; the half-cell potentials are subtracted in like manner. Thus



The sign of the voltage developed by the cell indicates the polarity of the right-hand electrode. If the sign is positive, it indicates that the reaction will proceed from left to right as written. On the other hand, if the sign is negative, the reaction will take place from right to left.

The magnitude of the voltage produced by a cell indicates the driving force of the reaction, or the relative energy level of one half-reaction as compared with the other half-reaction.

¹ Half-cell potentials cannot be added directly unless the result is a complete reaction.

TABLE 6-4 STANDARD OXIDATION-REDUCTION POTENTIALS

Half-cell reaction	E° , volts
$\text{Li} \rightleftharpoons \text{Li}^{+} + e$	3.02
$\text{K} \rightleftharpoons \text{K}^{+} + e$	2.92
$\text{Ba} \rightleftharpoons \text{Ba}^{++} + 2e$	2.90
$\text{Ca} \rightleftharpoons \text{Ca}^{++} + 2e$	2.87
$\text{Na} \rightleftharpoons \text{Na}^{+} + e$	2.71
$\text{Mg} \rightleftharpoons \text{Mg}^{++} + 2e$	2.34
$\text{Al} \rightleftharpoons \text{Al}^{3+} + 3e$	1.67
$\text{Mn} \rightleftharpoons \text{Mn}^{++} + 2e$	1.05
$\text{Zn} \rightleftharpoons \text{Zn}^{++} + 2e$	0.76
$\text{Cr} \rightleftharpoons \text{Cr}^{3+} + 3e$	0.71
$\text{S}^{-} \rightleftharpoons \text{S} + 2e$	0.51
$\text{H}_2\text{C}_2\text{O}_4(aq) + 2\text{H}_2\text{O} \rightleftharpoons 2\text{CO}_2(g) + 2\text{H}_3\text{O}^{+} + 2e$	0.49
$\text{Fe} \rightleftharpoons \text{Fe}^{++} + 2e$	0.44
$\text{H}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{O}^{+} (10^{-7}) + 2e$	0.41
$\text{Cr}^{++} \rightleftharpoons \text{Cr}^{3+} + e$	0.41
$\text{Cd} \rightleftharpoons \text{Cd}^{++} + 2e$	0.40
$\text{Co} \rightleftharpoons \text{Co}^{++} + 2e$	0.28
$\text{Ni} \rightleftharpoons \text{Ni}^{++} + 2e$	0.25
$\text{Sn} \rightleftharpoons \text{Sn}^{++} + 2e$	0.14
$\text{Pb} \rightleftharpoons \text{Pb}^{++} + 2e$	0.13
$\text{H}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{O}^{+} + 2e$	0.00
$\text{H}_2\text{S} + 2\text{H}_2\text{O} \rightleftharpoons \text{S} + 2\text{H}_3\text{O}^{+} + 2e$	-0.14
$\text{Sn}^{++} \rightleftharpoons \text{Sn}^{4+} + 2e$	-0.15
$\text{Cu}^{+} \rightleftharpoons \text{Cu}^{++} + e$	-0.17
$\text{Cl}^{-} + \text{Ag} \rightleftharpoons \text{AgCl} + e$	-0.22
$2\text{Cl}^{-} + 2\text{Hg} \rightleftharpoons \text{Hg}_2\text{Cl}_2 + 2e$	-0.27
$\text{Cu} \rightleftharpoons \text{Cu}^{++} + 2e$	-0.34
$2\text{I}^{-} \rightleftharpoons \text{I}_2 + 2e$	-0.54
$3\text{I}^{-} \rightleftharpoons \text{I}_3^{-} + 2e$	-0.54
$4\text{H}_2\text{O} + \text{HAsO}_2 \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}_3\text{O}^{+} + 2e$	-0.56
$\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 2\text{H}_3\text{O}^{+} + 2e$	-0.68
$\text{Fe}^{++} \rightleftharpoons \text{Fe}^{3+} + e$	-0.77
$2\text{Hg} \rightleftharpoons \text{Hg}_2^{++} + 2e$	-0.80
$\text{Ag} \rightleftharpoons \text{Ag}^{+} + e$	-0.80
$\text{Hg} \rightleftharpoons \text{Hg}^{++} + 2e$	-0.85
$\text{CuI} \rightleftharpoons \text{Cu}^{++} + \text{I}^{-} + e$	-0.88
$\text{Hg}_2^{++} \rightleftharpoons 2\text{Hg}^{++} + 2e$	-0.91
$\text{HNO}_2 + 4\text{H}_2\text{O} \rightleftharpoons \text{NO}_3^{-} + 3\text{H}_3\text{O}^{+} + 2e$	-0.94
$\text{NO} + 6\text{H}_2\text{O} \rightleftharpoons \text{NO}_3^{-} + 4\text{H}_3\text{O}^{+} + 3e$	-0.96
$2\text{Br}^{-} \rightleftharpoons \text{Br}_2(l) + 2e$	-1.07
$2\text{Br}^{-} \rightleftharpoons \text{Br}_2(aq) + 2e$	-1.09
$\text{I}_2 + 18\text{H}_2\text{O} \rightleftharpoons 2\text{IO}_3^{-} + 12\text{H}_3\text{O}^{+} + 10e$	-1.20
$6\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}_3\text{O}^{+} + 4e$	-1.23
$6\text{H}_2\text{O} + \text{Mn}^{++} \rightleftharpoons \text{MnO}_2 + 4\text{H}_3\text{O}^{+} + 2e$	-1.28
$2\text{Cl}^{-} \rightleftharpoons \text{Cl}_2(g) + 2e$	-1.36
$21\text{H}_2\text{O} + 2\text{Cr}^{3+} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + 14\text{H}_3\text{O}^{+} + 6e$	-1.36
$\text{Au} \rightleftharpoons \text{Au}^{3+} + 3e$	-1.42
$9\text{H}_2\text{O} + \text{Br}^{-} \rightleftharpoons \text{BrO}_3^{-} + 6\text{H}_3\text{O}^{+} + 6e$	-1.44

TABLE 6.4 STANDARD OXIDATION-REDUCTION POTENTIALS (*Continued*)

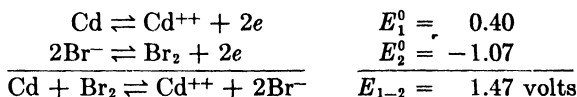
Half-cell reaction	E° , volts
$9\text{H}_2\text{O} + \text{Cl}^- \rightleftharpoons \text{ClO}_3^- + 6\text{H}_3\text{O}^+ + 6e$	-1.45
$12\text{H}_2\text{O} + \text{Mn}^{++} \rightleftharpoons \text{MnO}_4^- + 8\text{H}_3\text{O}^+ + 5e$	-1.52
$\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+} + e$	-1.61
$6\text{H}_2\text{O} + \text{MnO}_2 \rightleftharpoons \text{MnO}_4^- + 4\text{H}_3\text{O}^+ + 3e$	-1.67
$4\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e$	-1.77
$\text{Co}^{++} \rightleftharpoons \text{Co}^{3+} + e$	-1.84
$2\text{SO}_4^{--} \rightleftharpoons \text{S}_2\text{O}_8^{--} + 2e$	-2.05
$2\text{F}^- \rightleftharpoons \text{F}_2(g) + 2e$	-2.85

6.21 Application of Standard Electrode Potentials. Table 6.4 indicates the relative tendencies for substances at standard state to lose or gain electrons. Those substances at the top of the table lose their electrons most easily and are therefore the strongest reducing agents. The substances at the bottom gain electrons most readily and are the strongest oxidizing agents. In this table elementary lithium is indicated as the most effective reducing agent and elementary fluorine as the strongest oxidizing agent. The table is sometimes called the *reactivity series*, since the reactivity of the metals decreases from top to bottom, while that of the nonmetals increases in the same direction.

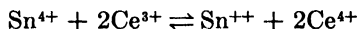
Standard electrode potentials may be used to calculate the emf of any cell whose reactants are at standard state. For example, given the cell



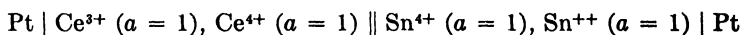
calculate the voltage produced and write the cell reaction.



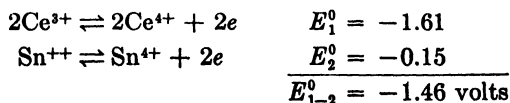
The table of standard electrode potentials permits the prediction as to whether a reaction (with reactants at standard state) will proceed as written. For example, will the reaction



take place from left to right as written? In constructing the cell for this reaction the reducing agent—the cerous ion—is arbitrarily set up as the left-hand cell. The construction of the cell is



The half-cell reactions and standard electrode potentials are



306 Fundamental Concepts of Inorganic Chemistry

The negative value obtained for the emf of this cell indicates that the chemical reaction obtained by combination of the half-cell reactions does not proceed in the direction as written but is spontaneous from right to left.

The potentials listed in Table 6.4 are not absolute values. They are relative half-cell potentials in terms of the standard hydrogen electrode, which is arbitrarily given a value of zero. For many reasons the construction and use of the hydrogen electrode are not always convenient. Consequently other reference electrodes have been devised whose emfs are accurately known in relation to the standard hydrogen electrode.

6.22 Effect of Concentration on Electromotive Force. Table 6.4 lists the standard electrode potentials of a number of half-cells at 25°C. These values are reproducible only when the substances which make up the half-cells are in their standard states of unit activity. If the substances are not at standard state, the electrode potentials are no longer standard electrode potentials. Therefore electrode potentials, at a fixed temperature, will vary with changing concentrations of the reactants which constitute the half-cells.

The relation of concentration to a single electrode potential is given by the Nernst equation,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{oxidised state}}}{a_{\text{reduced state}}}$$

where E is the measured electrode potential, E^0 is the standard electrode potential, n is the number of electrons involved in the half-cell reaction, R is in joules per degree (8.314), T is temperature in degrees Kelvin, F is the faraday constant (96,494 coulombs), and $a_{\text{ox}}/a_{\text{red}}$ is the ratio of the product of the activities of the reaction products divided by the product of the activities of the reactants, each activity raised to a numerical power equal to the coefficient of the number of ions involved in the half-cell equation. If all the constants are substituted into the equation at 25°C, it may be simplified to

$$E = E^0 - \frac{0.059}{n} \log \frac{a_{\text{ox}}}{a_{\text{red}}}$$

The emf of a cell in which the reactants of the half-cells are not at unit activity is expressed by the equation

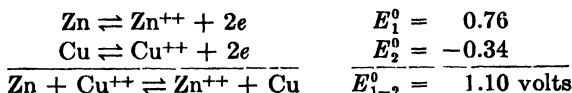
$$E_{1-2} = E^0_{1-2} - \frac{0.059}{n} \log Q$$

where Q is the product of the activities of the reaction products divided by the product of the activities of the starting substances, each activity raised to a numerical power equal to the coefficient of the number of molecules or ions involved in the chemical equation. By way of illustra-

tion this mathematical equation may be used for calculating the emf of a Daniel cell in which the concentration of the Cu^{++} is 0.001 F and that of the Zn^{++} is 1 F . The cell is set up as follows:



The half-cell reactions and the standard electrode potentials are

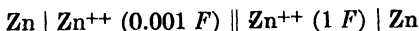


Therefore
$$E = 1.10 - \frac{0.059}{n} \log \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]}$$

where the concentration of the solid metals zinc and copper remains constant. Thus

$$\begin{aligned} E &= 1.10 - 0.0295 \log \frac{(1)}{(0.001)} \\ &= 1.01 \text{ volts} \end{aligned}$$

Since the potential difference between a metal and its ions depends upon ionic concentration, a cell can be constructed consisting of two electrodes of the same metal dipping into solutions of different ionic concentrations. This is one type of concentration cell, which may be illustrated by measuring the potential between two zinc electrodes whose ionic concentrations are 1 F and 0.001 F , respectively. This cell is indicated symbolically as



If the two half-cells are designated as E_1 and E_2 , then

$$\begin{aligned} E_1 &= E^0 - \frac{0.059}{2} \log 0.001 \\ E_2 &= E^0 - \frac{0.059}{2} \log 1 \end{aligned}$$

Combining the two equations produces

$$\begin{aligned} E_{1-2} &= - \frac{0.059}{2} (\log 0.001 - \log 1) \\ &= 0.088 \text{ volt} \end{aligned}$$

6.23 Calculation of Equilibrium Constants from Electrode Potentials.

Oxidation-reduction reactions are reversible and therefore subject to the law of chemical equilibrium. Consequently, when a cell is short-circuited until the voltage decreases to zero, the products and reactants of the half-cells reach a condition of concentrations in which they are in equilibrium with each other. At equilibrium, E_{1-2} is zero, and the Nernst equation

308 Fundamental Concepts of Inorganic Chemistry

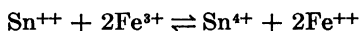
for determining the emf of a cell is modified into the expression

$$0 = E_{1-2}^0 - \frac{0.059}{n} \log K_*$$

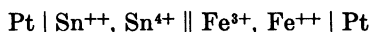
where K_* is the equilibrium constant for the cell reaction. Further simplification reduces the equation to

$$\log K_* = \frac{nE_{1-2}^0}{0.059}$$

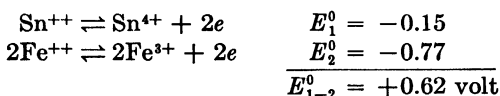
This expression permits the calculation of equilibrium constants from the electrode potentials of the half-cells involved in redox reactions. To illustrate, consider the reaction



from which the following cell may be set up:



The half-cell reactions and standard electrode potentials are



At equilibrium
$$0 = 0.62 - \frac{0.059}{2} \log K_*$$

$$K_* = 10^{21}$$

The magnitude of the equilibrium constant of a reaction is an approximate indication of the completeness of the reaction under specified conditions. It is also an approximation of the driving force of the reaction. A large value for K_* indicates that the reaction goes, from left to right, a long way toward completion. The same general significance holds true for a very small equilibrium constant, except that such a value indicates that the reaction proceeds from right to left. When two standard potentials are not very different, the equilibrium constant which may be derived from the two half-cell reactions will not vary widely from unity. Such a value indicates that the over-all cell reaction will not be complete in either direction.

Since the magnitude and sign of an equilibrium constant indicates the extent and course of a chemical reaction, it is to be expected that there is a direct relation between free-energy changes (driving forces) and equilibrium constants. This relationship is expressed in the equation

$$\text{Change in free energy} = -RT \ln K$$

where R is a constant equal to 1.988 cal and T is temperature in degrees

Kelvin. The use of this equation may be illustrated by the reaction between zinc and copper ions. In Sec. 6-16 the free-energy change for the reaction was calculated as $-51,020$ cal; therefore, at 25°C , the equilibrium constant may be obtained as

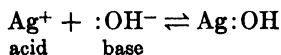
$$\begin{aligned} -51,020 \text{ cal} &= -1.988 \times 298 \times \ln K \\ K &= 10^{37} \end{aligned}$$

This relationship is extremely convenient as a means of recording equilibrium constants with a small number of entries. A table of standard free energies of a large number of substances can be recorded on a few pages, whereas a tabulation of the equilibrium constants involving these same substances would require hundreds of pages.

It should be pointed out that the evaluation of an equilibrium constant from two standard electrode potentials is not always a trustworthy indication of the completeness of the cell reaction. A wide difference in electrode potentials denotes that the reaction will proceed until the concentrations of the reactants are greatly altered, but this difference gives no information as to the rate at which equilibrium is approached. It is possible that the absence of a suitable catalyst may prevent such a reaction from reaching equilibrium within a reasonable time.

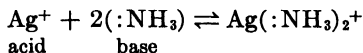
6-24 The Relation between Oxidation-Reduction and Acid-Base Reactions. In Sec. 6-13 we defined the processes of oxidation and reduction in terms of electron gain and electron loss. A reducing agent was described as an electron donor and an oxidizing agent as an electron acceptor. The driving force of a redox reaction is the affinity of the oxidizing agent for electrons. In a somewhat analogous fashion the G. N. Lewis interpretation of acids and bases describes a base as any substance having a pair of electrons which it can donate to establish a coordinate bond and an acid as any substance which may accept an electron pair to form such a bond. Again, the driving force of the reaction is the affinity of the acid for electrons. The close relationship between oxidation-reduction and acid-base reactions is clearly indicated. Both acids and oxidizing agents exhibit an affinity for electrons. To this extent they are both described as being *electrophilic* (electron-loving) in their nature. In like manner, bases and reducing agents are designated as *electrodotic*, or electron-giving, agents.

The analogy between the two types of reactions leads to the expectation that a reactant may display either oxidation-reduction or acid-base properties depending upon the substance with which it reacts. An excellent example of behavior of this kind is the action of the silver ion as either an acid or an oxidizing agent. In its reaction with the hydroxide ion,

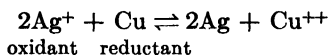


310 Fundamental Concepts of Inorganic Chemistry

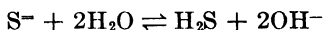
the silver ion acts as an acid in accepting a pair of electrons from the hydroxide ion. It reacts similarly with ammonia,



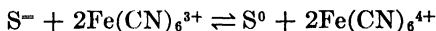
to accept electron pairs from ammonia molecules to form two coordinate bonds. Toward reducing agents the silver ion behaves as an oxidizing agent. In the latter capacity the silver ion may oxidize certain metals, such as copper, to their ions, as, for example,



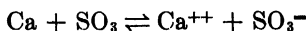
In a similar fashion the sulfide ion may behave as either a base or a reducing agent, depending upon its reaction partner. In its reaction with the water molecule the sulfide ion furnishes two electrons to produce two hydroxide ions,



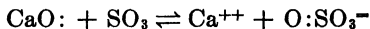
On the other hand it acts as a reductant toward certain oxidizing agents, e.g., the ferricyanide ion,



However, the donor-acceptor concept of acid-base reactions does differ from the electron transfers involved in redox reactions. The former consists in a more or less unequal sharing, whereas the latter is a complete transfer. This difference may be illustrated by examining the mechanism of the reaction of SO_3 with Ca and comparing it with the reaction of SO_3 with CaO. In the former, calcium acts as an oxidizing agent to donate a pair of electrons to the sulfur trioxide molecule. The pair of electrons are transferred completely from the metal to the molecule, and the resulting products are two charged particles.



The reaction between sulfur trioxide and calcium oxide is one of neutralization in which the pair of electrons involved in the reaction are shared mutually between the sulfur and the oxygen atoms within the sulfate ions.



The distinction between the reactions of Lewis acids and bases and those of oxidation and reduction is a matter of definitions, involving the transfer or sharing of an electron pair. This difference does not exist in the Usanovich treatment (Sec. 6·10). This concept includes both types of reactions as acid-base systems, and no differentiation is made between them.

EXERCISES

1. Give an explanation for the fact that polar solids have a limit to their solubilities in water, whereas polar liquids may be miscible in all proportions.
2. Why is mercuric chloride more soluble in benzene than is barium chloride?
3. Why will sugar dissolve in water but not in benzene?
4. Why are the liquids carbon tetrachloride and water miscible? Why, then, are the liquids alcohol and water miscible in all proportions?
5. What is the relation of the dielectric constant of the solvent to the solubility of an ionic compound?
6. To what extent is the melting point of a substance an indication of its solubility in water?
7. Strong hydrogen bonds exist between fluoride ions in a water solution of hydrogen fluoride. Why is the same not true between chloride ions in a water solution of hydrogen chloride?
8. In spite of its limitations the Arrhenius explanation of acid-base systems is usually satisfactory for an elementary discussion of aqueous solutions. Give reasons for this statement.
9. In what ways does the Lewis interpretation of acid-base systems differ from the Brønsted-Lowry concept?
10. The ammonia molecule has a pyramidal structure, with the three N-H bonds forming angles of 109° . Predict, with explanation, the expected solubility of true salts in liquid ammonia.
11. The fluoride atom has a small radius. How does this fact affect the degree of ionization of hydrofluoric acid?
12. In each of the following acid pairs predict which acid should be stronger in aqueous solution, and give reasons for your choice:
 - (a) Selenic acid or sulfuric acid
 - (b) Telluric acid or sulfurous acid
 - (c) Hydrogen sulfide or hydrogen telluride
13. In water solutions is HCO_3^- stronger as an acid or as a base? Why?
14. Arrange the following acids in the order of their decreasing acidities, and state reasons for the assigned order: HOBr , HOCl , and HOI .
15. In each of the following base-pairs, predict which base should be the stronger in aqueous solution, and give reasons for your choice:
 - (a) Potassium hydroxide or barium hydroxide
 - (b) Beryllium hydroxide or strontium hydroxide
 - (c) Ferrous hydroxide or ferric hydroxide
16. Assign oxidation numbers to the elements in the following compounds: Fe_3O_4 , RuO_4 , Ag_2F , CuFeS_2 , $\text{K}_3\text{Fe}(\text{CN})_6$, K_2PtCl_6 , $\text{H}_2\text{C}_2\text{O}_4$, Hg_2Cl_2 , NH_4NO_2 , and H_2SO_5 .
17. Why is HClO a better oxidizing agent than HClO_4 ?
18. What factors determine the difference of potential which may exist between a metal and its ions?
19. What does the numerical value of an equilibrium constant indicate concerning the completeness of a reaction?
20. The following unbalanced equations represent redox reactions taking place

312 Fundamental Concepts of Inorganic Chemistry

in acid solutions. Convert them to balanced ionic equations, introducing hydronium ions and water molecules wherever necessary.

- (a) $\text{Fe}^{++} + \text{ClO}_3^- \rightleftharpoons \text{Fe}^{3+} + \text{Cl}^-$
- (b) $\text{Cr}_2\text{O}_7^{--} + \text{NO}_2^- \rightleftharpoons \text{Cr}^{3+} + \text{NO}_3^-$
- (c) $\text{MnO}_4^- + \text{Fe}^{++} \rightleftharpoons \text{Mn}^{++} + \text{Cl}_2$
- (d) $\text{Cr}^{3+} + \text{S}_2\text{O}_8^{--} \rightleftharpoons \text{Cr}_2\text{O}_7^{--} + \text{SO}_4^{--}$
- (e) $\text{BrO}_3^- + \text{I}^- \rightleftharpoons \text{Br}^- + \text{I}_2$

21. The following equations represent cell reactions in which all reactants and products are at standard state. Construct the cell and determine the voltage for each reaction.

- (a) $\text{Mg} + 2\text{Ag}^+ \rightleftharpoons \text{Mg}^{++} + 2\text{Ag}$
- (b) $2\text{I}^- + \text{Cl}_2 \rightleftharpoons \text{I}_2 + 2\text{Cl}^-$
- (c) $2\text{Fe}^{3+} + 2\text{Br}^- \rightleftharpoons 2\text{Fe}^{++} + \text{Br}_2$

22. Calculate the voltage at 25°C, and write the cell reaction for each of the following cells:

- (a) $\text{Pb} \mid \text{Pb}^{++} (1 F) \parallel \text{Ag}^+ (1 F) \mid \text{Ag}$
- (b) $\text{Pt} \mid \text{I}_2, \text{I}^- (1 F) \parallel \text{Ce}^{4+} (1 F), \text{Ce}^{3+} (1 F) \mid \text{Pt}$

23. Calculate the equilibrium constant for each of the following reactions:

- (a) $\text{Sn}^{4+} + \text{Pb} \rightleftharpoons \text{Pb}^{++} + \text{Sn}^{++}$
- (b) $2\text{Fe}^{++} + 2\text{I}^- \rightleftharpoons 2\text{Fe}^{++} + \text{I}_2$

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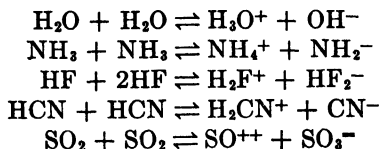
CHAPTER 7

Inorganic Substances in Nonaqueous Media

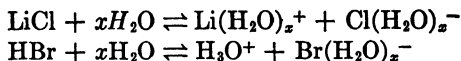
Water has long been recognized as the "universal solvent." This recognition is due largely to the plentiful occurrence of water in nature and its unusual solvating characteristics. No other solvent is quite so versatile in terms of availability, wide liquid range, ease of handling, and ability to dissolve substances. No other solvent displays so wide a range in physical and chemical properties. For these many reasons water occupies an exceptional position among solvating media. However, we hasten to add that water is not unique in its properties. Many other substances have similar solvent properties, but it must be admitted that such properties are not usually so pronounced as in water. The difference between water and certain other solvents is more often a matter of degree rather than a difference in behavior. Unfortunately very few liquids have been investigated as to their behavior as solvents for inorganic substances. It is doubtful that any other branch of inorganic chemistry offers wider opportunities for investigation than does the study of inorganic substances in nonaqueous media.

Many liquids have the ability to dissolve inorganic materials, but we are more interested in those solutions in which ionic reactions take place. Solvents in which ionization takes place may be described as possessing "waterlike" properties, and it is upon the basis of such properties that solvents are sometimes classified.

7.1 The Properties of Ionizing Solvents. It is believed that all ionizing media exist as ions, to some extent, when in the pure state; consequently such solvents are invariably weak conductors of electricity. Familiar examples of solvents of this type are water, liquid ammonia, hydrogen fluoride, liquid hydrogen cyanide, and liquid sulfur dioxide. The ionization reactions by which these compounds produce charge-bearing particles are postulated as



Ionizing solvents are usually polar compounds (Secs. 4·16 and 6·2). Such a compound is composed of molecules in which there is some separation of positive and negative charges. It is probable that polar solvent molecules align themselves in a manner so as to weaken interionic attraction within ionic crystals and thereby draw ions into solution. The solvating tendencies of polar compounds may also serve to rupture covalent bonds, as is evidenced by the reaction of water with hydrogen chloride to produce ionization. There is a direct correlation between the magnitude of the dipole moment of a solvent and its solvating ability. If the dipole moment is large, it is to be expected that the solvent molecules will react with ionic or polar solutes quite readily. Equations exemplifying reactions between polar solvents and ionic and polar solutes are



An ionizing solvent not only has a large dipole moment but also has a high dielectric constant. The two properties are closely related. The magnitude of the dipole moment, or polarity, depends upon the distance separating the two charges within a molecule and may be evaluated by multiplying the distance between the centers of the two charges by the value of one of the charges. On the other hand the dielectric constant of a solvent is determined by the extent to which its molecules, when placed in an electric field, orient themselves in a manner to neutralize the field. A vacuum is arbitrarily assigned a value of unity. Hence a large value for the dipole moment of a solvent also indicates a large value for its dielectric constant. The close correlation between the two properties is given in Table 7·1.

An ionic compound is composed of positive ions interspaced with negative ions. The forces operating between the oppositely charged particles have a profound influence upon the pattern and physical properties of the crystal lattice. Many ionic compounds enter solution because the dipole forces produced by the molecules of a polar solvent weaken the electrostatic forces between the ions within the crystal. Consequently, when a pair of oppositely charged ions leave a crystal, the effective force between the two charges is considerably weakened. Furthermore the extent to which the attractive force is reduced is inversely proportional to the dielectric constant. Mathematically the attractive force within

the solution is only $1/e$ of the force operating within a vacuum, provided the distance between the ions remains unchanged. The symbol e represents the dielectric constant of the solvent. Coulomb's law for two charged bodies in a medium of dielectric constant e becomes

$$F = \frac{1}{e} \frac{q_1 q_2}{r^2}$$

where F is the force of attraction between the two ions with charges q_1 and q_2 and r is the distance between the centers of the two particles. It

TABLE 7-1 DIPOLE MOMENTS AND DIELECTRIC CONSTANTS OF SOME IONIZING SOLVENTS

Solvent	Dipole moment*	Dielectric constant†
Water.....	1.84	78.5 (25°C)
Ammonia.....	1.46	22 (-33.5°C)
Hydrogen fluoride...	1.9	83.6 (0°C)
Hydrogen cyanide.....	2.93	106.8 (25°C)
Sulfur dioxide.....	1.61	17.27 (-16.5°C)

* In Debye units; 1 Debye unit = $1 \text{ D} = 10^{-18}$ esu.

† Nonpolar liquids have dielectric constants of the order of 2.

should be remembered (Sec. 4-6) that Coulomb's law represents only the electrostatic energy between the two ions, whereas in an ionic crystal or ionic solution the same two ions are subjected to additional coulombic forces from other ions. However, the foregoing equation represents a qualitative indication of what happens when an ionic compound dissolves in a polar solvent. Accordingly a solvent with a large dielectric constant is expected to be a good solvent for an electrovalent compound, and the solution process is one in which the attraction between ions is weakened. Conversely it may be predicted that solvents with small dielectric constants are poor solvents for ionic substances.

The dipole charges within polar molecules give rise to the phenomenon of association. This is a condition where the various molecules with oppositely charged ends attract each other to produce rings, chains, or clusters. Association appears frequently in protonic solvents where hydrogen bonding (Sec. 4-25) is possible. Solvents with associated structures have unexpectedly high boiling points and, consequently, wide liquid ranges. Associated liquids are good solvents of either salts or polar compounds. For a substance to be soluble in an associated solvent, it must be able to tear apart or penetrate the associated structure. Ions, because of their large charges, are able to attract polar molecules

of a solvent and, in doing so, rupture the associating bonds sufficiently to enter the intermolecular spaces of the solvent. Polar solutes either react with the solvent molecules or substitute themselves into the associated structure of the solvent. Nonpolar solutes do not dissolve in polar solvents because of the "squeezing-out" effect produced by the associated structure of the latter. The problem of solubility has been discussed in Chap. 6. However, it seems worthwhile to repeat a common rule relating to solubility which states that "like dissolves like."

Another pronounced property of waterlike solvents is their leveling effect (Sec. 6-11) upon strong acids. It will be recalled that such solvents react more or less completely with strong acids, leaving only hydronium ions in solution; consequently the acids appear to have equal strength. It is also true that one concept of acid-base behavior (Sec. 6-7) is based upon the explanation of solvent reactions with certain solutes.

7-2 Classification of Solvents. Solvents have been classified in a number of ways. Obviously all such arrangements depend upon some particular chemical or physical property or upon some series of these properties. Among the various groups which have been suggested are:

Protonic and Aprotic Solvents. This separation refers back to the Brønsted idea of acid-base behavior. Protonic solvents are those which contain hydrogen from which protons may be derived, e.g., water and liquid ammonia. Aprotic solvents are those from which protons are not ordinarily obtained and may be exemplified by the compounds carbon tetrachloride and benzene.

Acid Solvents, Basic Solvents, Amphiprotic Solvents, and Aprotic Solvents. Among those solvents which are classified as acid are glacial acetic acid and liquid hydrogen fluoride. Basic solvents are illustrated by liquid ammonia and ethylenediamine. Amphiprotic solvents include those which have no decidedly acid or basic properties, such as the lower alcohols and water. Aprotic solvents are nonprotonic compounds, among which benzene and carbon tetrachloride are good examples.

Ionizing and Nonionizing Solvents. This classification is based upon the polar or nonpolar nature of the solvents. The properties of ionizing solvents have been described in Sec. 7-1, and examples of this type are listed in Table 7-1. Nonionizing solvents are those with low dielectric constants, and again we use benzene and carbon tetrachloride to typify such liquids.

Despite the distinguishing properties which serve as a basis for the various classifications of solvents, none of these classifications has any particular merit for our discussion. As we stated in our introduction to this chapter, the investigation of nonaqueous solvents has been largely limited to a few dozen compounds, and any attempt to classify such meager information in a systematic manner would not add to its clarifica-

tion. It seems just as well to follow the example of the majority of writers and simply examine those nonaqueous systems, one by one, which have been explored to the greatest extent.

LIQUID AMMONIA

7.3 Liquid Ammonia as a Solvent. No other nonaqueous solvent has been exploited as extensively as ammonia. Its availability, ease of handling, and waterlike properties have contributed to its use as a solvent. Liquid ammonia shows a striking resemblance to water in its solvent action. It is less strongly associated through hydrogen bonding, and consequently the freezing and boiling points are lower than those of water. The fact that its dielectric constant is 22 as compared with 78.5 for water is a contributing factor to ammonia's inability to dissolve as many salts as water. On the other hand ammonia is a better solvent than water for molecules containing many electrons, such as iodine compounds, and for nonpolar substances, as exemplified by the hydrocarbons. Its solvent action upon covalent compounds has resulted in more extensive exploration of reactions involving organic substances than those relating to inorganic materials. However, our present discussion will be limited to reactions of the latter type.

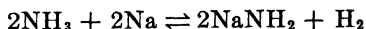
One remarkable difference between the solvent actions of liquid ammonia and water is the former's ability to dissolve the alkali metals without apparent chemical action. The resulting solutions possess a characteristic deep blue color, and the dissolved metals may be recovered unchanged by simply allowing the solvent to evaporate. The alkaline earth metals also dissolve in liquid ammonia, but the solvent action is probably chemical since evaporation of the solvent yields the metal in the form of a hexammonate, $M \cdot (NH_3)_6$.

Inasmuch as the physical properties of liquid ammonia differ in many respects from those of water, it is to be expected that the solvent action of the two liquids toward various salts should be somewhat dissimilar. Among the soluble inorganic compounds that dissolve in liquid ammonia are the nitrates, nitrites, thiocyanates, and most cyanides. The majority of fluorides are insoluble, as are oxides, hydroxides, sulfates, carbonates, phosphates, sulfites, and most sulfides. Among the halides, other than the fluorides, solubility decreases from the iodide to the chloride. Most iodides are soluble, the bromides are somewhat less soluble, and among the chlorides only the ammonium, beryllium, and sodium compounds can be classified as soluble. The nature of the anion seems to affect the solubilities of various salts in liquid ammonia even more than in the case of water. The only general exception to this statement is the solubility of the ammonium ion, whose salts are all soluble in liquid

ammonia regardless of the anion to which the ammonium group is attached. By way of illustration, reducing agents stronger than hydrogen will liberate this element from water, whereas solutions of the alkali and alkaline earth metals in liquid ammonia provide strong reducing systems in which the solvent is unaffected. Another advantage of ammonia over water as a solvent is the lesser tendency of ammonia to enter into reaction (solvolysis) with a dissolved solute.

The greatest disadvantage in the use of liquid ammonia as a solvent and reaction medium is the elaborate equipment and special techniques which are necessary because of ammonia's physical properties. The boiling point of pure ammonia is -33.35°C ; therefore, it is necessary to work at low temperatures if high pressures are to be avoided. Another disadvantage is the fact that ammonia is an extremely hygroscopic liquid, and great care must be taken to prevent atmospheric moisture from penetrating an ammonia system under study.

7.4 Solutions of Metals in Liquid Ammonia. Liquid ammonia has a relatively low degree of autoionization. By this description we mean that pure liquid ammonia does not ionize within itself to any great extent, despite the ionization reaction indicated in Sec. 7.1. For this reason solutions of alkali metals in liquid ammonia are stable even at room temperature over an extended period of time. Eventually the following reaction occurs to some extent:



The presence of small amounts of certain catalysts, such as iron oxide, will cause the reaction to take place rapidly.

The blue solutions of metals in liquid ammonia are unique in that they conduct an electric current metallically. In highly concentrated solutions the conductance may approach that of the free metal, whereas, in a dilute solution, the electric conductivity is of the magnitude of an electrolytic solution. Conductance measurements also show that the "anion" is the same irrespective of the metal dissolved, and any differences in equivalent conductance values can be attributed to the nature of the cation. The latter, of course, depends upon the metal which is in solution.

A clue to the process by which metals may dissolve in ammonia is afforded by the fact that only those metals which lose electrons very easily will dissolve in ammonia. The electron affinity of these metals is quite low, and if they enter solution by loss of electrons, then the solvation energy necessary to bring about solution must likewise be low. It is now believed that the blue solutions of metals in liquid ammonia contain the metallic ions and free electrons. Moreover the blue color that is present in these metal solutions can be attributed to the presence of free electrons. One theory postulates that the electrons are trapped

in cavities which they have created throughout the liquid. The cavities are assumed to be of a size very close to that of a single ammonia molecule.

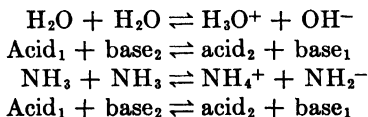
The view that metals enter solution in liquid ammonia by loss of electrons,



indicates that the dissolution is to some extent a chemical process, inasmuch as electrons are lost. Furthermore the fact that the metals may be reclaimed by evaporation of the solvent shows that the electrons are returned to their parent ions. The metallic conductance of such solutions bears evidence of the presence of free electrons. It is also true that these same free electrons render their solutions among our most powerful reducing agents.

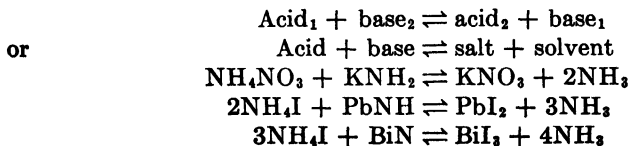
7.5 Reactions in Liquid Ammonia. Since ammonia has waterlike properties as a solvent, it is not unexpected that chemical reactions which take place in ammonia solution closely parallel those which occur in aqueous solution. Certainly it is convenient to classify and discuss the reactions which have been investigated in liquid ammonia as the same general types which take place in water. Accordingly such reactions may be grouped under the following five headings: (1) acid-base reactions, (2) redox reactions, (3) precipitation reactions, (4) complex formations, and (5) solvolysis reactions.

Acid-Base Reactions. According to the Brønsted concept of acids and bases the ionization reactions which take place in water and ammonia are similar.



and

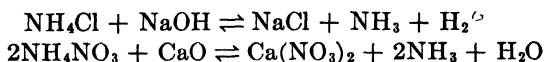
From the second reaction it may be deduced that the ammonium ion is an acid and the amide ion is a base in liquid ammonia. Consequently it is to be anticipated that ammonium salts will act as acids in liquid ammonia, whereas amides, imides, or nitriles will behave as bases in the same medium. In terms of the Brønsted definitions neutralization is a process in which an acid and base react to produce another acid and base. Neutralization has also been defined as a reaction between an acid and base to produce a salt and the solvent. Regardless of the definition the following reactions in liquid ammonia may be regarded as neutralization reactions:



320 Fundamental Concepts of Inorganic Chemistry

In the foregoing reactions ammonium salts are to be considered as acids, the amide as a monoacidic base, the imide as a diacidic base, and the nitride as a triacidic base. The course of neutralization reactions in liquid ammonia may be followed by means of conductimetric titrations, and in certain cases through the use of indicators. By way of illustration, phenolphthalein is colorless in liquid ammonia but develops an intense red color in the presence of alkali amides. Consequently the alkali amides may be titrated in liquid ammonia with ammonium salts using phenolphthalein as an indicator.

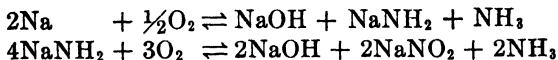
The acidic nature of ammonium salts in liquid ammonia is further revealed by the fact that they are able to dissolve metal oxides and hydroxides. Such reactions may be considered as acid-base phenomena, of which the following cases are typical:



Ammonium salts in liquid ammonia react with active metals with the evolution of hydrogen. Although the acidity of the ammonium ion is clearly indicated, a reaction of this kind can hardly be classified as acid-base activity.

Redox Reactions. Oxidation-reduction reactions take place in liquid ammonia just as they do in water. In fact many of the investigations involving inorganic substances in liquid ammonia have been concerned with actions which have been described as reduction processes. However, the process of reduction cannot occur without that of oxidation taking place at the same time. Nevertheless we find that the concept of oxidation-reduction as occurring in ammonia is rather obscure. About all we can do to shed light upon the problem is to find illustrations which will exemplify certain definitions.

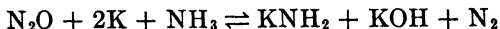
When gaseous oxygen is passed slowly through a solution of metallic sodium in liquid ammonia, the first products are the hydroxide and amide, followed later by further oxidation in which the amide is converted into the nitrite.



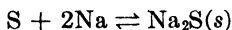
Solutions of alkali and alkaline earth metals in liquid ammonia may act as electron donors (reducing agents) by yielding their conducting electrons to electron acceptors (oxidizing agents). Hence the action of metallic sodium in liquid ammonia with ammonium bromide is essentially an oxidation-reduction reaction.



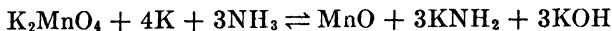
Nitrous oxide oxidizes metallic potassium in liquid ammonia to the potassium ion and is itself reduced to nitrogen in the process.



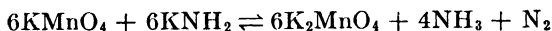
Hundreds of reactions involving the reducing action of metals in liquid ammonia have been investigated. It is noteworthy that these reductions may include either elements or compounds and that the substances may be metals, nonmetals, or salts. For example, elemental sulfur reacts with sodium in liquid ammonia to form the sulfide ion, which subsequently precipitates as white, crystalline sodium sulfide.



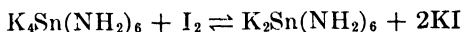
The oxidizing action of potassium permanganate in liquid ammonia is considerably weaker than in water solutions. Potassium permanganate is reduced rapidly to K_2MnO_4 and the oxides of manganese when treated with a solution of potassium in liquid ammonia. This reduction is followed by a slower reaction in which the manganate is further reduced to MnO . The latter action may be indicated by the equation



It is also of interest that potassium permanganate is reduced to the manganate by a liquid ammonia solution of potassium amide.



In liquid ammonia elementary iodine acts as a weak oxidizing agent in oxidizing potassium ammonostannite to the ammonostannate. The equation for this action is



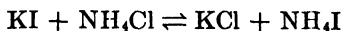
The solutions of metals in liquid ammonia are powerful reducing agents, presumably because of the free electrons existing in solution, which are easily available to electron acceptors. These reducing solutions have been widely exploited in organic chemistry to bring about many reactions that would otherwise be impossible. On the other hand very strong oxidizing agents apparently do not exist in liquid ammonia. For example, nitric acid (ammonium nitrate) in liquid ammonia is not an oxidizing agent, and permanganates and chromates exhibit only weak oxidizing powers.

Precipitation Reactions. The precipitation reactions of ionized substances in liquid ammonia proceed in the same manner as those which occur in water solution. Consequently, when two ions that are capable of forming a slightly soluble compound come in contact with each other, a precipitate results. However, the compounds which are insoluble in

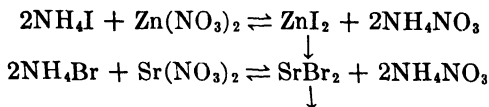
322 Fundamental Concepts of Inorganic Chemistry

liquid ammonia vary considerably from those which are insoluble in water. Some of the anions which form insoluble compounds in ammonia are listed in Sec. 7-3.

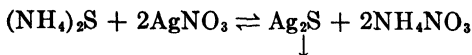
Most chlorides are insoluble in liquid ammonia. Exceptions are sodium, ammonium, and beryllium chlorides. If liquid ammonia solutions of potassium iodide and ammonium chloride are brought together, a white precipitate of potassium chloride is produced.



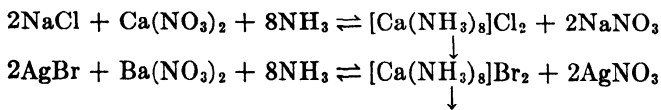
Most nitrates are soluble in liquid ammonia, and this fact is used in certain precipitation methods. Thus the addition of the nitrates of a number of metals to solutions of ammonium iodide or ammonium bromide causes the precipitation of the metal in question with the particular anion. Equations for these reactions are



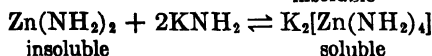
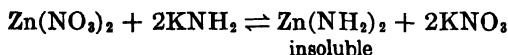
Ammonium sulfide, dissolved in liquid ammonia, will precipitate the sulfides of various metals.



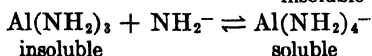
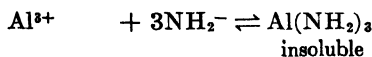
Many insoluble halides are precipitated not as the simple halides but as the complex amines, which in the water system correspond to compounds containing water of crystallization. Examples of precipitations of this type are



Complex Formations. The possibilities of complex formations in liquid ammonia systems have not been explored fully. Some of those which have been investigated are quite similar to complex formations occurring in the water system. For example, in aqueous solution, the addition of cyanide ions to silver ions precipitates insoluble silver cyanide. The insoluble precipitate dissolves in excess cyanide ions due to the formation of the soluble complex ion $\text{Ag}(\text{CN})_2^-$. Analogous reactions take place in liquid ammonia. Thus zinc ions may be precipitated as insoluble zinc amide, which dissolves in excess amide to form the ammonozincate. Molecular equations for these reactions are



Aluminum amalgam reacts similarly to form a soluble complex ion, the ammonoaluminate. The ionic equations are



Solvolysis Reactions. These reactions are usually referred to as *ammonolysis*, or *ammonolytic reactions*, and may be defined as metathetical (replacement) reactions in which ammonia is a reactant. Reactions of this type are analogous to the familiar hydrolysis reactions of

TABLE 7-2 AMMONOLYSIS REACTIONS INVOLVING INORGANIC HALIDES
Substance Ammonolytic product

AuCl	AuCl·12NH ₃
HgCl ₂	HgNH ₂ Cl
BCl ₃	B(NH ₂) ₃
AlI ₃	AlI ₃ ·6NH ₃
SiCl ₄	Si(NH ₂) ₄
SiH ₃ Cl	(SiH ₃) ₃ N
GeCl ₄	Ge(NH) ₂
SnCl ₄	2Sn(NH ₂) ₃ Cl·NH ₄ Cl
PbI ₂	PbNH·Pb(NH ₂)I
TiCl ₄	TiNCl·xNH ₃
ZrBr ₄	3Zr(NH) ₂ ·7NH ₄ Br·xNH ₃
NOCl	NONH ₂
PCl ₃	P(NH ₂) ₃ , P ₂ (NH) ₃
PCl ₅	P(NH) ₂ NH ₂
PBr ₃	P(NH ₂) ₃
AsX ₃ *	As(NH ₂) ₃
SbCl ₃	SbN
VOCl ₃	VO(NH ₂) ₃
VCl ₃	[V(NH ₂) ₆]Cl ₃
TaCl ₅	Ta(NH ₂) ₂ Cl ₃ ·3NH ₃
TeBr ₄	Te ₂ N ₄
CrCl ₃	[Cr(NH ₂) ₄]Cl ₃ , [Cr(NH ₂) ₃]Cl ₂
MoCl ₅	Mo(NH) ₂ NH ₂ or Mo(NH ₂) ₄ Cl

* X is Cl, Br, I.

water. In other words, an ammonolytic reaction is one of double decomposition in which ammonia is a reactant.

An ammonolytic reaction, familiar to most chemists, is the action of ammonia on mercurous chloride.



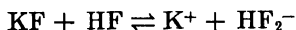
Ammonolysis reactions, including both inorganic and organic substances, have been investigated extensively. A summary of early investigations has been compiled by Fernelius and Bowman.¹ From this excellent summary a few typical examples of ammonolysis involving inorganic materials have been selected, and these are given in tabular form in Table 7-2.

LIQUID HYDROGEN FLUORIDE

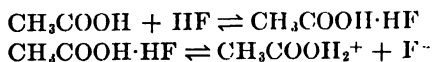
7-6 Liquid Hydrogen Fluoride as a Solvent. The physical properties of liquid hydrogen fluoride are similar to those of water. It melts at -83°C and boils at 19.4°C . It is a highly associated liquid with a high dielectric constant and possesses fairly good solvent properties. However, it dissolves fewer salts unchanged than does water. The lower solvating power may be attributed to a difference in chemical properties rather than a dissimilarity in physical behavior. The extreme chemical reactivity of hydrogen fluoride restricts a comparison of its solvent action with those of water and ammonia. In fact its chemical activity is so pronounced that very few anions can dissolve in it without change.

The dissolution of a solute in liquid hydrogen fluoride may proceed along one of four different courses:

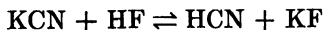
1. Dissociation into ions in a manner similar to that which occurs in other ionizing solvents. This behavior may be illustrated by the solvent action upon potassium fluoride.



2. Chemical addition of HF to the solute, followed by a dissociation which produces a complex ion and the fluoride ion. The action of hydrogen fluoride with acetic acid exemplifies these reactions.



3. Chemical reaction resulting in the replacement of the anion of the solute with the fluoride. The action of hydrogen fluoride with potassium cyanide, in which HCN is liberated, illustrates this exchange.



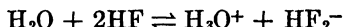
4. Chemical reaction involving more than simple replacement. This type of dissolution occurs when hydrogen fluoride reacts with sulfuric acid to produce fluosulfonic acid, hydronium ions, and fluoride ions.



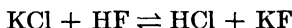
¹ W. C. Fernelius and G. B. Bowman, Ammonolysis in Liquid Ammonia, *Chem. Revs.*, **26**: 3 (1940).

The foregoing possibilities of solvent action indicate that simple dissolution of a solute in hydrogen fluoride is less frequent than other actions. Consequently very few salts dissolve in liquid hydrogen fluoride to yield their simple ions. A few generalities as to the action of inorganic materials with this solvent may be made.

Oxides and hydroxides usually react violently with liquid hydrogen fluoride to form the fluoride ion and water. Water reacts with excess solvent to give hydronium and bifluoride ions.

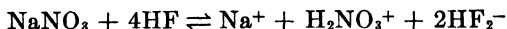


The majority of chlorides, bromides, and iodides are either insoluble and unaffected or react with the solvent to evolve the hydrogen halide. The latter action is illustrated by the behavior of the solvent with potassium chloride.



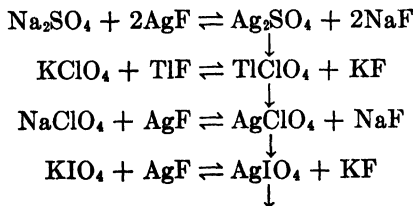
Sodium and potassium sulfates are readily soluble, being converted first into sulfuric acid and then to fluosulfonic acid (the latter reaction has been given). Most other sulfates are insoluble.

Nitric acid and a few nitrates are soluble. The solvating action of hydrogen fluoride upon these substances produces the aquonitronium and bifluoride ions.



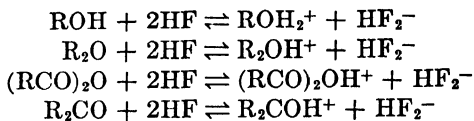
Only fluorides, fluoborates, and perchlorates dissolve in liquid hydrogen fluoride to give the same ions that they produce in water. Therefore it may be said that only three of the common anions can exist in both solutions: the ClO_4^- ion, the BF_4^- ion, and the HF_2^- ion.

7.7 Reactions in Liquid Hydrogen Fluoride. Since only a few anions are stable in liquid hydrogen fluoride, reactions corresponding to neutralization and precipitation are uncommon. Despite a previous statement that only three anions are stable in the solvent, a few other anions such as the sulfate and periodate are sufficiently stable to produce precipitations. Some of the precipitation reactions which may occur in liquid hydrogen fluoride are indicated in the following molecular equations:



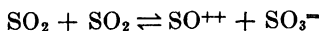
326 Fundamental Concepts of Inorganic Chemistry

Many organic compounds dissolve in liquid hydrogen fluoride to give solutions with high electric conductivity. It is believed that the solvating reaction is one in which the organic molecule accepts a proton to form a complex positive ion. Reactions of this type occur with alcohols, phenols, ethers, aldehydes, acids, acid anhydrides, and others. A few representative equations are



LIQUID SULFUR DIOXIDE

7.8 Liquid Sulfur Dioxide as a Solvent. This "waterlike" solvent boils at -10°C and freezes at -75.5°C ; consequently the liquid range is sufficiently high to permit its use as a solvent. The pure liquid is a poor conductor, but it apparently ionizes slightly according to the equation



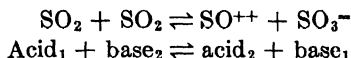
Although it has a dipole moment of 1.61 D, its liquid range and molecular weight suggest that liquid sulfur dioxide is not associated to any great extent as compared with the other solvents which have been discussed. The weak association can be attributed to the lack of hydrogen in its make-up. (It is believed that hydrogen bonding is largely responsible for association in liquids.) The dielectric constant of liquid sulfur dioxide is 17.27, which, although much lower than that of water, accounts for its ability to dissolve a number of salts. Moreover the fact that these salt solutions show a high conductivity to an electric current proves that the solvent is an ionizing medium.

The solubilities of inorganic materials in liquid sulfur dioxide vary over a wide range, and it is impossible to make broad generalities concerning these solubilities which do not involve many exceptions. Except for the iodides most solubilities are low, being of an order of 0.2 to 2.0 g/100 ml. Alkali and alkaline earth metal iodides are quite soluble, but the solubilities of these metals decrease rapidly through the bromides, chlorides, and fluorides. Because of the reverse order of solubility for the alkali halides in sulfur dioxide and ammonia, it is possible to use these two solvents for the separation of cesium and rubidium from the other alkali metal ions. Many salts of ammonium, thallium, and mercuric mercury are soluble. In addition to the salts already named the sulfites and acetates of the alkali metals are soluble, as well as many thiocyanates and cyanides. A solubility table of salts in liquid sulfur dioxide has been

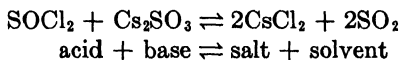
compiled by Pray.¹ Of the salts with higher solubilities many form addition compounds with the solvent. Examples of such molecular compounds are $\text{NaI} \cdot 4\text{SO}_2$, $\text{KI} \cdot 4\text{SO}_2$, $\text{BaI}_2 \cdot 4\text{SO}_2$, $\text{LiI} \cdot 2\text{SO}_2$, $\text{AlCl}_3 \cdot \text{SO}_2$, and $\text{KCNS} \cdot \text{SO}_2$. The nonelectrolytes thionyl chloride, SOCl_2 , and thionyl acetate, $\text{SO}(\text{OOCCH}_3)_2$, mix with sulfur dioxide in all proportions. Liquid sulfur dioxide is also an excellent solvent for many organic compounds and serves as a medium for such organic reactions as the Friedel-Crafts, sulfonation, and bromination types. In fact the liquid is a better solvent for covalent compounds than for electrovalent materials. Industrial use is made of its solvent properties in the purification of certain petroleum products.

7.9 Reactions in Liquid Sulfur Dioxide. It is convenient to describe reactions occurring in liquid sulfur dioxide in terms of the various types of similar actions that take place in water. Among the reactions that have been observed in the former liquid are five types which also occur in water, namely, acid-base reactions, redox reactions, precipitation reactions, complex formations, and solvolysis reactions.

Acid-Base Reactions. An examination of the apparent autoionization of liquid sulfur dioxide indicates that the thionyl ion should be an acid and the sulfite ion a base. According to Brønsted definitions the equation may be written



By analogy thionyl chloride can be classified as an acid and cesium sulfite as a base. These two substances are soluble in liquid sulfur dioxide and react in this medium with acid-base characteristics to form cesium chloride and the solvent. The molecular equation for the reaction is



The reaction may be followed conductimetrically to produce a typical neutralization curve.

Oxidation-Reduction Reactions. At high temperatures gaseous sulfur dioxide may behave either as an oxidizing agent or as a reducing agent, depending upon the substance with which it reacts. On the other hand liquid sulfur dioxide does not have any pronounced oxidizing or reducing properties, although it may serve as a medium for oxidation-reduction reactions. Not many redox systems have been investigated in liquid sulfur dioxide. Among the few that have been discovered are the oxidizing actions of certain metallic ions upon soluble iodides. The interaction

¹ A. R. Pray, *Nonaqueous Chemistry*, "Comprehensive Inorganic Chemistry," vol. 5, pt. II, p. 191, D. Van Nostrand Company, Inc., Princeton, N.J., 1956.

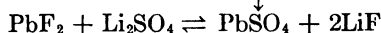
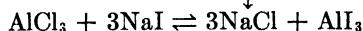
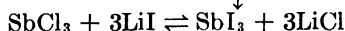
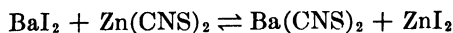
328 Fundamental Concepts of Inorganic Chemistry

between potassium iodide and antimony pentachloride illustrates reactions of this type. The molecular equation may be written as

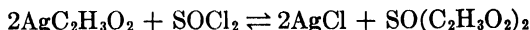


The course of the reaction may be followed by conductimetric titration.

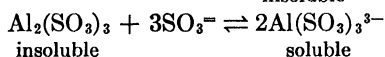
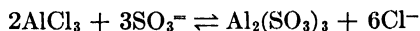
Precipitation Reactions. The use of solubility relationships permits an extensive number of precipitations to be carried out in liquid sulfur dioxide. Equations illustrating the precipitations of several insoluble materials upon the mixing of soluble compounds are as follows:



The miscibility of thionyl chloride in liquid sulfur dioxide may be utilized in the preparation of new thionyl derivatives. In reactions of this type the precipitation of an insoluble compound can be used to displace one thionyl acid by another. For example,



Complex Formations. The mode of formation of many complex ions in liquid sulfur dioxide is frequently analogous to the process occurring in aqueous solutions. Typical behavior of this kind is the solubility of a precipitate in an excess of its own anion. Examples of such reactions in liquid sulfur dioxide are the precipitate and soluble complex formed between the aluminum ion and the sulfite ion.

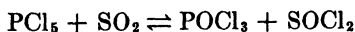


Another complex formation, not involving a precipitate, is the interaction between antimony trichloride and potassium chloride, both of which are soluble, to give the soluble complex K_3SbCl_6 .



Solvolysis Reactions. As was stated in the preceding section, high solubilities of salts in liquid sulfur dioxide are quite often the result of solvation. Among solvates of this type not already mentioned are $\text{RbI} \cdot 3\text{SO}_2$, $\text{SrI}_2 \cdot 4\text{SO}_2$, and $2\text{TiBr}_4 \cdot \text{SO}_2$.

Solvolysis reactions have been obtained with certain halides. By way of illustration, phosphorus pentachloride reacts readily with liquid sulfur dioxide to form phosphorus oxychloride.



Other halides may react similarly if heated with the solvent in a sealed tube.

LIQUID HYDROGEN CYANIDE

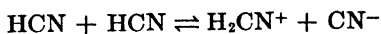
7-10 Liquid Hydrogen Cyanide as a Solvent. In respect to those physical properties which are believed to contribute to the solvating power of a liquid toward salts, hydrogen cyanide should be the best of all solvents. It boils at 25.6°C, which is abnormally high for a compound with so low a molecular weight, indicating a high degree of association through hydrogen bonding. It has the highest dielectric constant of any liquid, being approached only by water and hydrogen fluoride. The dipole moment of liquid hydrogen cyanide is 2.93, which is higher than any other "waterlike" solvent. All told, this liquid should be the best of all ionizing media. Most of the substances that dissolve and ionize in water should do the same in liquid hydrogen cyanide. However, these expectations do not turn out to be true. Hydrogen cyanide is not an unusual solvent; in fact it is definitely inferior to water as a solvating medium.

The poisonous nature of hydrogen cyanide has been a deterring factor to its use as a solvent and will probably be a hampering influence on future investigations. For this reason the solubility data concerning hydrogen cyanide solutions are too incomplete for trustworthy conclusions. Nevertheless it may be said that hydrogen cyanide not only dissolves various electrovalent compounds but appears to be even a better solvent for certain covalent substances. A few salts of the alkali metals are either soluble or sparingly soluble. Among these are NaCl, KCl, NH₄Cl, NaNO₃, KCl, K₂SO₄, and KI. Many covalent chlorides are soluble and produce ions in the solvating process, for example, POCl₃, SOCl₂, BiCl₃, SbCl₅, and HCl. Other halides that dissolve without ionization are SnCl₄, SnBr₄, SnI₄, and I₂. Many organic compounds are readily soluble. A few of the more common among such compounds are benzene, aniline, methanol, glycerin, urea, and ethanol.

7-11 Reactions in Liquid Hydrogen Cyanide. Insufficient data are available concerning chemical reactions in liquid hydrogen cyanide to permit a worthwhile comparison of these reactions with similar ones in aqueous solution. Inasmuch as the autoionization reaction of hydrogen

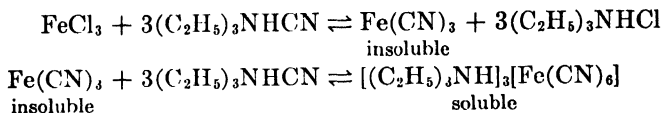
330 Fundamental Concepts of Inorganic Chemistry

cyanide appears to be

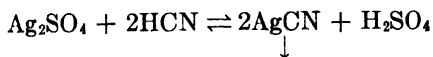


those substances furnishing protons in solutions should act as acids and soluble compounds that produce cyanide ions ought to behave as bases. Consequently it is not surprising that soluble acids (for example, H_2SO_4 , HNO_3 , HCl , and dichloroacetic acid) may be neutralized by cyanide ions in *acid-base reactions*. These neutralization reactions may be followed by means of conductimetric titrations or in some cases by indicators which change color in liquid hydrogen cyanide.

As in water solutions *complex formations* may sometimes take place in hydrogen cyanide upon the addition of an excess of a precipitating agent. The interaction between ferric chloride and triethylammonium cyanide in liquid hydrogen cyanide serves to illustrate one mode of complex formation. The first addition of triethylammonium cyanide to ferric chloride solution, gives a precipitate of ferric cyanide, which dissolves upon addition of an excess of the precipitating reagent. The precipitate and soluble complex are indicated in the following equations:



A few *solvolysis reactions* have been observed in liquid hydrogen cyanide. A typical example is the reaction between silver sulfate and hydrogen cyanide to produce insoluble silver cyanide and sulfuric acid. The equation for the reaction is



ACETIC ACID

7.12 Acetic Acid as a Solvent. The exploitation of acetic acid as a solvent has been largely a matter of convenience. It cannot be classed as a waterlike solvent, but it does have physical properties that make it convenient to use in the laboratory. Its liquid range is between 16.6 and 118°C; it is nontoxic and stable under ordinary laboratory conditions. The greatest difficulty encountered in its use is the preparation of anhydrous acetic acid. Simple distillation is not sufficient to remove all the water from acetic acid, and the special methods which must be employed to remove water are arduous and exacting.

Although acetic acid is associated, it has a dipole moment of zero. This unusual combination of properties results from the fact that as a

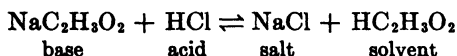
liquid it exists in the form of a dimer (Sec. 4-25). Certainly the dimeric structure accounts for its high boiling point, and to some extent for other unexpected properties. Its dielectric constant is 7.14, which is quite low as compared with the solvents that have been described as possessing waterlike characteristics (Table 7-1). In view of the properties which have been listed it might be expected that acetic acid would be a very poor solvent for ionic compounds. However, a surprisingly large number of salts are soluble in this solvent.

There is a wide variation in the solubility of salts in acetic acid. A series of qualitative tests have been made by A. W. Davidson,¹ and the results of his findings are given in Table 7-3.

TABLE 7-3 THE SOLUBILITY OF VARIOUS SALTS IN ACETIC ACID

Readily soluble	Sparingly soluble	Slightly soluble	Practically insoluble
LiNO ₃	AgNO ₃	NaCl	AgCl
Ca(NO ₃) ₂	AlCl ₃	KCl	AgBr
NH ₄ NO ₃	HgCl ₂	KBr	AgI
Cu(NO ₃) ₂	HgI ₂	KI	AgCN
CaCl ₂	CoCl ₂	NH ₄ Cl	AgCNS
ZnCl ₂		NH ₄ Br	PbCl ₂
SbCl ₃		NH ₄ I	PbI ₂
FeCl ₃		NaNO ₃	Hg ₂ Cl ₂
BaI ₂		KNO ₃	CdI ₂
ZnI ₂		BaCl ₂	Ba(NO ₃) ₂
NH ₄ CNS		KClO ₃	Ca ₃ (PO ₄) ₂
KCN		Na ₂ SO ₄	Cu ₃ (PO ₄) ₂
LiC ₂ H ₃ O ₂		(NH ₄) ₂ SO ₄	CaCO ₃
KC ₂ H ₃ O ₂		Cu(C ₂ H ₃ O ₂) ₂	Zn(C ₂ H ₃ O ₂) ₂
NH ₄ C ₂ H ₃ O ₂			All sulfates not listed
Pb(C ₂ H ₃ O ₂) ₂			
Cd(C ₂ H ₃ O ₂) ₂			

7-13 Reactions in Acetic Acid. Certain types of reactions which are found in aqueous solution may also occur in acetic acid. Typical *acid-base* reactions take place between soluble acetates and the so-called "strong" acids. In a reaction between sodium acetate and hydrochloric acid the acetate ion acts as a base, and the proton is the acid. The neutralization reaction may be expressed in the equation

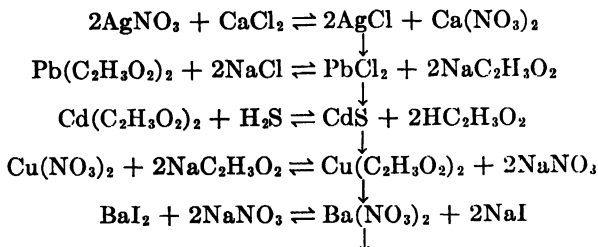


The variation in solubility among various salts in acetic acid, as indicated in Table 7-3, suggests that many metathetical reactions are possible

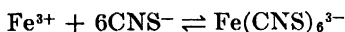
¹ A. W. Davidson, *J. Am. Chem. Soc.*, **50**: 1890 (1928).

332 Fundamental Concepts of Inorganic Chemistry

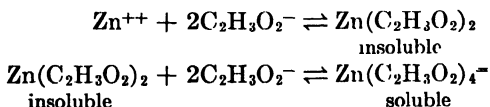
because of differences in solubility. Some of the many precipitation reactions which have been observed are given in the following molecular equations:



Complex formations in acetic acid solution are analogous to those happening in water solution. For instance, the reaction between ammonium thiocyanate and ferric chloride in an acetic acid medium produces the same red-colored complex that may be formed in aqueous solution.



Other soluble complexes are produced by the addition of an excess of a precipitating anion in certain interactions. Examples of such reactions are indicated by ionic equations as



OTHER NONAQUEOUS SOLVENTS

A desirable solvent should be a liquid with a wide liquid range under ordinary laboratory conditions of temperature and pressure. It should be easily available, convenient to handle, and nontoxic in nature. Furthermore, to bring about dissolution among ionic compounds, it must be a polar compound with a high dielectric constant. Very few solvents possess many of these desirable characteristics. Quite a number of compounds having one or more of these qualities have been investigated as solvating mediums, but the field of nonaqueous solvents is far from being adequately explored. Among the systems that have been investigated are those involving liquid hydrogen sulfide, liquid phosgene, selenium oxychloride, anhydrous sulfuric acid, anhydrous nitric acid, liquid nitrosyl chloride, and liquid bromine trifluoride. We shall examine only the first three systems in this list.

7.14 Liquid Hydrogen Sulfide as a Solvent. The positions of oxygen and sulfur in the periodic table would indicate that H_2O and H_2S should

be analogous compounds, and it might be expected that these two chemically related substances should have similar physical properties. This predicted similarity does not turn out to be true. Hydrogen sulfide is a poisonous gas at ordinary conditions of temperature and pressure. It is a liquid between -85 and -60°C , which is inconveniently low for experimental work, and within a narrow range of temperature. It has a dielectric constant of 10.2 at -60°C and a dipole moment of 1.18 D. Liquid hydrogen sulfide is a much poorer solvent for ionic compounds than is water; however, it is not satisfactory to attempt a comparison of two systems in which the difference in the liquid-temperature ranges is so

TABLE 7-4 SOLVOLYSIS OF A NUMBER OF HALIDES IN LIQUID HYDROGEN SULFIDE

<i>Reacting solute</i>	<i>Product of solvolysis</i>
SnCl_4	SnS_2^*
PCl_3	P_2S_3
PCl_5	PSCl_3
AsCl_3	As_2S_3
SbCl_5	SbSCl_3
HgCl_2	HgS
Hg_2Cl_2	$\text{Hg}_2(\text{SH})_2$

* Slow reaction.

great. If water could be supercooled to -60°C it might have a low dielectric constant and be a poor solvent of ionic substances at that temperature. On the other hand it seems certain that hydrogen sulfide is not associated to any great extent, because of the low temperature necessary for its liquefaction. In this connection it should be remembered that most good ionizing media are highly associated.

Substances that produce solutions with liquid hydrogen sulfide may be divided into three groups:

1. Compounds that enter solution without apparent reaction. This group consists chiefly of organic substances and certain covalent inorganic materials. Among the latter may be listed hydrogen chloride, hydrogen bromide, aluminum chloride, arsenic trisulfide, and antimony trisulfide.

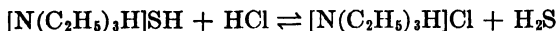
2. In the second group are soluble compounds that react with the solvent. The reaction is usually caused by one of three things: the oxidizing power of the solute, the fact that the solute contains an amino group, or because thiohydrolysis takes place. Solutes exemplifying these three factors are pyrosulfuric acid, aniline, and phosphorus trichloride.

3. The third group is made up of those elements and compounds which are insoluble in liquid hydrogen sulfide but which may go into solution because of chemical action. Elements and compounds of this group are sodium, copper, sodium peroxide, and silver nitrate.

A few *acid-base* reactions have been observed in liquid hydrogen sulfide. One neutralization which has been investigated in this medium is the

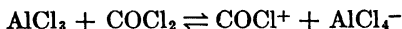
334 Fundamental Concepts of Inorganic Chemistry

action of hydrogen chloride with triethylammonium hydrosulfide. The equation may be written as



A number of *solvolysis* reactions have been studied in liquid hydrogen sulfide. Table 7-4 lists a few halides that react with liquid hydrogen sulfide, and the products of the solvolysis reactions.

7-15 Liquid Phosgene as a Solvent. Liquid phosgene, also known as *carbonyl chloride*, COCl_2 has a liquid range between -118 and $+8^\circ\text{C}$. Its dipole moment is 1.18 D, and its dielectric constant is relatively small. The boiling point and molecular weight indicate that little, if any, association is present in the liquid state. Liquid phosgene is a poor solvent of inorganic substances, and it is of interest in our present discussion because it serves as a nonprotonic solvent for certain acid-base reactions (Sec. 6-7). The pure solvent is a poor conductor of electricity, but it dissolves anhydrous aluminum chloride—another nonconductor—to give a conducting solution. It has been postulated that the ionization reaction follows a course indicated by the equation



Electrolysis of this solution yields carbon monoxide at the cathode and chlorine at the anode. The solution also reacts with various active metals, such as calcium, magnesium, potassium, and zinc. One possible equation for activity of this kind is



Although aluminum chloride is the only solute which has been studied in detail, other covalent halides are soluble in the same solvent. Among these soluble or miscible substances are SbCl_3 , SbCl_5 , S_2Cl_2 , SCl_2 , ICl_3 , and I_2 .

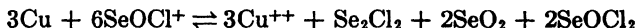
7-16 Selenium Oxychloride as a Solvent. This solvent has a liquid range between 8 and 177°C . Although its electric conductivity is low, it has a high dielectric constant which is of the same order of magnitude as that of water. It has been suggested that the autoionization of selenium oxychloride may proceed according to the following equation:



Electrolysis of the pure solvent or of a solution, such as one containing KCl , yields chlorine at the anode and a mixture of products at the cathode. Among the latter are selenium oxychloride, selenium dioxide, and selenium chloride.

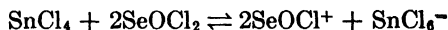
Among the various salts that dissolve in selenium oxychloride to produce conducting solutions are KCl , NaCl , NH_4Cl , BaCl_2 , HgCl_2 , and FeCl_3 . Metals may react with selenium oxychloride to give products

similar to those liberated at the cathode during electrolysis. For example,



A number of compounds form solvates with selenium oxychloride. These solvates may be classified as either acids or bases depending upon their behavior in acid-base reactions. Among those substances which form bases with the solvent are the alkali metal chlorides, as well as certain organic materials such as pyridine and quinoline. Some of the compounds that produce acids with the solvent are the chlorides of silicon, titanium, tin, arsenic, and iron, and also sulfur trioxide. Several potentiometric titrations have been carried out between these acids and bases. A few of the systems that have been investigated are those of $\text{C}_6\text{H}_5\text{N-SnCl}_4$, KCl-SnCl_4 , $\text{CaCl}_2\text{-SnCl}_4$, $\text{C}_6\text{H}_5\text{N-FeCl}_3$, $\text{C}_6\text{H}_5\text{N-SO}_3$, and $\text{C}_6\text{H}_5\text{N-AsCl}_3$. Of the solvates which have been studied, potassium chloride has been found to be the weakest base, followed by pyridine and quinoline, whereas sulfur trioxide appears to be the strongest acid, followed by the chlorides of iron and tin.

Selenium oxychloride resembles liquid phosgene in its solvent properties. The former reacts with stannic chloride to give a conducting solution in much the same fashion as the reaction between phosgene and aluminum chloride. The equation for the selenium oxychloride interaction may be postulated as



The analogy between the solution of stannic chloride in selenium oxychloride and that of aluminum chloride in liquid phosgene continues with the behavior of the two solutions toward active metals. Such metals are far more soluble in the stannic chloride and aluminum chloride solutions than in the solvents alone.

EXERCISES

1. Suggest reasons for the slow progress in exploring the use of nonaqueous solvents for inorganic reactions.
2. What physical properties must a liquid possess in order that it produce ionization in a solution of an ionic compound?
3. Is it necessary for a solvent to be a proton donor in order that it may be an ionizing medium?
4. Define and explain what is meant by dielectric constant as applied to liquids.
5. Why are nonpolar compounds usually insoluble in strongly polar solvents?
6. What is the relation between the dipole moment of a liquid and its solvating power?
7. Strong oxidizing agents apparently do not exist in liquid ammonia. Give the reasons underlying this statement.

336 Fundamental Concepts of Inorganic Chemistry

8. Write a possible equation for the complexing action of liquid ammonia upon a soluble compound of lead.
9. Explain the powerful reducing action of solutions of alkali metals in liquid ammonia.
10. Discuss the resemblance of inorganic reactions in liquid ammonia to those which occur in water.
11. Alkali metals react with water but dissolve without chemical action in liquid ammonia. Give reasons for this difference in behavior.
12. List some advantages possessed by liquid ammonia over water as a reaction medium.
13. Why is liquid ammonia a better solvent for organic compounds than is water?
14. Why is liquid ammonia less associated than is water?
15. Account for the instability of most anions in liquid hydrogen fluoride.
16. Describe the various ways in which salts may enter into solution in liquid hydrogen fluoride.
17. Despite its higher dielectric constant, fewer salts dissolve in liquid hydrogen fluoride than in water. Give reasons for this lower solvating power.
18. It has been said that liquid hydrogen fluoride has more pronounced water-like properties than does water itself. Explain the basis for this statement.
19. Why are iodide salts more soluble in liquid sulfur dioxide than are salts of any other anion?
20. Suggest reasons for the reverse order of solubility for the alkali halides in sulfur dioxide and ammonia.
21. Why are salts, as a whole, less soluble in liquid sulfur dioxide than in water?
22. Sulfur dioxide gas is easily liquefied under pressure. What physical properties are responsible for the ease of liquefaction?
23. Hydrogen sulfate dissolved in liquid hydrogen cyanide behaves as a tri-basic acid. This behavior is assumed to be a result of solvation. Write an equation for such a solvation.
24. Suggest reasons why liquid hydrogen cyanide is inferior to water as a solvent for ionic compounds.
25. Acetic acid has a different leveling effect upon strong acids. Explain what is meant by this statement.
26. Explain how it is possible for the dipole moment of acetic acid to be zero in view of the fact that the molecule has an unsymmetrical structure.
27. Suggest methods for removing water from acetic acid.
28. Why is liquid hydrogen sulfide a better solvent for organic and covalent compounds than for ionic substances?
29. Write the equation for the autoionization reaction of liquid hydrogen sulfide.

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CHAPTER 8

Radioactivity and Nuclear Transformation

In many respects our final chapter is a supplement to the first. Both chapters are concerned with atomic nuclei, but whereas the first chapter dealt largely with nuclear structure and problems relating to nuclear composition, our last chapter will be devoted to changes which occur in the nuclei of atoms, with special emphasis upon the chemical aspects of these changes. In this chapter we shall consider nuclear reactions that convert atoms of one element into atoms of another, or "transmutation," as it is sometimes called. Transmutation takes place naturally, although usually at a very slow rate, among certain heavy elements. It may be brought about artificially, and frequently at a rapid rate, by bombarding nuclei with various missiles. Transmutation may also be accomplished through fusion of very light elements to form a less energetic element such as helium. Nuclear reactions produce a multiplicity of new isotopes, stable and unstable, some of which are isotopes of elements occurring in nature, and others of elements which do not occur in nature and which were unknown until recently. The chemical and physical properties of the new elements are of theoretical interest, and many of the new radioactive isotopes are of industrial and biological importance. These are some of the items that we shall discuss in this chapter.

NATURAL RADIOACTIVITY

Radioactivity is a process in which the nuclei of certain elements undergo spontaneous disintegration, and the rate of decay is characteristic of the particular isotope concerned. Furthermore the breaking down of unstable nuclei of active isotopes to produce other isotopes is accompanied by the emission of radiation. The type of ray emitted provides a clue to the nuclear transformation. All the heavy elements from bismuth through uranium, and a few of the lighter elements, have naturally radioactive isotopes.

8-1 Discovery of Radioactivity. In a series of experiments designed to find some relation between X rays and fluorescence Henri Becquerel in 1896 accidentally discovered the phenomenon of radioactivity. It should be added, incidentally, that this property of certain nuclei was discovered long before anyone suspected that atoms might have nuclei. Becquerel's experiments were initiated as a result of the discovery of X rays by Röntgen a year earlier. Shortly after the discovery H. Poincaré made the observation that X rays apparently originate in the luminescent spot produced where cathode rays impinge upon the glass of the Crookes tube. This suggestion stimulated Becquerel to investigate the possibility that fluorescent salts of uranium might emit radiations similar in nature to X rays. Both Henri Becquerel and his father, Edmond Becquerel, had previously been interested in a type of luminescence known as *fluorescence* as exhibited by certain minerals, and Henri Becquerel had in his possession a specimen of potassium uranyl sulfate which had been used in the study of fluorescence. This sample was used in his now famous experiment.

The uranium salt was exposed to the action of sunlight while resting upon a photographic plate, the latter being wrapped in black paper to protect it from the light. When the plate was developed, the portion which had been directly under the uranium salt was found to be blackened. In similar experiments Becquerel discovered that the rays from the uranium salt could pass through thin sheets of aluminum and copper and still blacken the photographic plate. The experiments seem to confirm Poincaré's idea of a relationship between luminescence and the production of X rays. However, in the course of these experiments, one photographic plate was exposed to the action of the uranium salt without the benefit of sunlight as the result of a cloudy day. The plate upon development exhibited the same blackening as previous plates, indicating that the uranium salt must have emitted rays capable of affecting a photographic plate in the absence of sunlight. Additional investigation showed that the rays possessed properties similar to X rays and proved that the emission was not dependent upon exposure to sunlight. Later it was learned that there is no relation between fluorescence and the emission of rays from a uranium salt, inasmuch as fluorescence of a salt ceases when the light source is removed. Thus an experiment designed for another purpose resulted in the discovery of the phenomenon of radioactivity. The term *radioactivity* was first used by Mme Curie, who later showed that the emission of radiation was a property not of the uranium salt but of the uranium atom.

In the course of his investigations with uranium compounds Becquerel discovered that the radiations from these substances are similar to X rays to the extent that they can penetrate materials opaque to ordinary light

and are able to discharge an electroscope. The latter is a device consisting of two strips of gold leaf suspended from the top of a glass container. Charged bodies, upon touching the top of the apparatus, impart a charge to the leaves, causing them to separate. This separation is caused by repulsion of like charges on the two leaves. Either X rays or radiations from radioactive compounds produce ionization in air, causing it to be a conductor. The presence of electrically charged particles in the air about an electroscope permits the charge on the leaves to leak away. Becquerel found that the intensity of radioactive emanations could be measured qualitatively by the rate of discharge occurring between the charged leaves of the electroscope.

In 1898 Marie Sklodowska Curie became interested in the quantitative measurement of radioactivity. Her husband Pierre Curie and his brother had discovered the property of piezoelectricity and from the discovery had invented an electrometer suited to the measurement of very small currents. Making use of this sensitive electrometer, Marie Curie was able to measure, quantitatively, the radiations produced by various uranium compounds. As a subject for her doctor's dissertation she undertook a systematic study of those substances which emit radiations. In this investigation she found that all compounds of uranium are radioactive, the extent of the activity being proportional to the amount of uranium in the substance. She also reported a similar activity in thorium compounds. In correlating radioactivity with percentage of uranium present in various uranium minerals, it was found that pitchblende from Jáchynov exhibited an activity several times greater than that of metallic uranium. This activity suggested that pitchblende must contain some other substance more highly radioactive than uranium. A search for a satisfactory explanation for the unusual radioactivity in pitchblende led Marie Curie and her husband to the discovery of two new elements, and resulting fame.

While seeking the ingredient responsible for the unexpected degree of radioactivity in pitchblende, Marie Curie, with the aid of her husband, succeeded in isolating a material which proved to be 400 times more active than uranium. It serves no useful purpose to describe the details of this extraction, but the main steps are of interest in that they follow the familiar Fresenius scheme of qualitative analysis. The pitchblende was dissolved in acids and the resulting solution treated with hydrogen sulfide. The uranium and thorium remained in solution and did not show any enhanced radioactivity. The sulfide precipitate contained lead, bismuth, antimony, copper, and arsenic, as well as a component that was highly radioactive. Ammonium sulfide was used to dissolve antimony and arsenic from the precipitate, and the resulting residue was dissolved in nitric acid. From this solution lead was precipitated as the

sulfate, and then ammonia was used to separate bismuth from copper. The precipitated bismuth hydroxide was found to contain most of the radioactive component.¹ The new element and bismuth were separated by heating their sulfides to about 700°C in an evacuated tube. Under these conditions the radioactive sulfide was deposited upon the cooler portions of the tube. In July, 1898, the Curies announced the discovery of a new element, which they named *polonium*, after Marie Curie's native land, Poland. This was the first element to be discovered and isolated through its property of radioactivity.

In another chemical extraction involving pitchblende the Curies with the aid of G. Bémont isolated another radioactive product in the form of a chloride. This substance exhibited an activity 900 times greater than uranium and resembled the alkaline earths in its chemical properties. The quantity of material was extremely small and greatly contaminated with barium chloride. However, spectrographic examination showed the presence of an unknown spectral line in addition to that of barium. In December, 1898, the Curies announced the discovery of a second radioactive element, which they called *radium* after the Latin word for ray.

8-2 Radioactive Emanations. While the Curies were conducting their epoch-making separations of pitchblende, Becquerel continued to investigate the properties of the radiations which he had discovered. In 1899 he observed that these radiations were deflected in a magnetic field in the same direction as cathode rays. This behavior indicated that the radiations contained negatively charged particles, electrically similar to cathode rays. Shortly afterward Ernest Rutherford, while studying the penetration of metal foils (Sec. 2-4) by radioactive radiations, arrived at the conclusion that the emanations were of two types, which he designated as *alpha* (α) rays and *beta* (β) rays. He characterized each by its deflection in a magnetic field and its range of power in penetrating solid bodies. A third type of radiation, which could not be deflected by a magnetic field but which had great penetrating power, was discovered by P. Villard of France in 1900. This group of radiations has since been named *gamma* (γ) rays. With the discovery of artificial radioactivity other products of nuclear disintegration have been recognized (Sec. 8-10). In the present discussion it seems worthwhile to examine more closely the characteristic properties of the three types of radiations which are the result of natural radioactivity.

Alpha rays are made up of electrically charged particles whose charge is twice as large as that on an electron and of opposite sign. The ratio of charge to mass has been calculated to be about half that of the hydrogen

¹ The bismuth hydroxide carrier separation was a precursor to the carrier analysis techniques which were to be used later so extensively in the analyses of trace quantities of short-lived radioactive substances, particularly the transuranic elements.

342 Fundamental Concepts of Inorganic Chemistry

ion; consequently an alpha particle has a mass within the magnitude of that of atoms. The mass may be estimated by the fact that alpha particles are only slightly deflected (in the direction of the negative pole) in a magnetic field and are stopped by thin layers of metal foil. Alpha particles have initial velocities ranging between 1.5 and 2.0×10^9 cm/sec, or approximately one-tenth the speed of light. The characteristic properties and behavior of alpha particles identified them as doubly charged helium ions. Later studies by Ramsay and Soddy showed helium to be one of the products of radioactive decay and proved that it is first emitted in the form of alpha radiation.

Since the mass and velocity of alpha particles are large, they possess great momentum; yet they can be stopped or completely absorbed by an aluminum foil less than $\frac{1}{10}$ mm in thickness. One of the first experiments with alpha particles (Sec. 2.4) showed that they can pass through very *thin* layers of metal foil, owing to their great momentum, and because the body of the foil is largely open space. From this experiment Rutherford concluded that atoms and matter are largely open structures which may be penetrated by high-speed particles. The absorption value of a metal foil depends not only upon its thickness but also upon the atomic weight of the foil. The higher its atomic weight, the greater is the absorption. Alpha particles are so large that they are also impeded by gases. The range of the particles in a gas depends upon the nature of the gas and is inversely proportional to the pressure and directly proportional to the absolute temperature. The particles may plow through only a few centimeters of air before their energies are dissipated. The impeding effect of a gas varies as the square root of its atomic weight; consequently alpha particles can penetrate four times farther in hydrogen than in oxygen.

The range of alpha particles in air is characteristic for the particular radioactive element from which they emanate. Furthermore the extent of the range is a qualitative indication of the life period of the element. Those elements which decay most rapidly emit alpha particles with the greatest ranges, while those elements that have the longest half lives (Sec. 8.4) give off rays with the smallest ranges. At 15°C and 1 atm pressure the range for thorium, Th^{232} , the longest-lived, is 2.9 cm, whereas the range for polonium, Po^{212} , the shortest-lived, is 8.6 cm. The ranges of alpha particles in air (at 15°C and 1 atm pressure), emitted by a number of radioactive elements, are given in Table 8.1. In the same table are recorded the half lives of the same elements in order to show the inverse relationship between range and half life.

Beta rays are high-speed electrons ejected from the nuclei of atoms of certain radioactive elements. A magnetic field deflects these particles in an opposite direction to that taken by alpha particles in the same field.

This behavior proves that the charges on the two different types of particles are opposite in sign. Beta corpuscles differ from ordinary electrons only in their tremendous velocities, which may range between 33 and 99 per cent that of light. Owing to variations in velocity, beta rays are not homogeneous, and deflection by a magnetic field produces a spectrum which is indicative of their source. Because of their extraordinary velocities, beta particles have far more penetrating power than alpha particles. They are largely absorbed by a layer of aluminum 5 mm thick. As in the case of alpha particles the stopping power of

TABLE 8-1 RANGES AND HALF LIVES OF ALPHA PARTICLES FOR A NUMBER OF NATURAL RADIOELEMENTS

Radioelement	Range,* cm	Half life
Thorium, Th ²³²	2.8	1.39×10^{10} years
Uranium, U ²³⁸	2.83	4.51×10^9 years
Uranium, U ²³⁴	2.9	2.33×10^5 years
Radium, Ra ²²⁶	3.3	1.59×10^3 years
Thorium, Th ²³⁰	3.9	1.9 years
Polonium, Po ²¹⁸	4.6	3.0 min
Polonium, Po ²¹⁶	5.6	0.16 sec
Polonium, Po ²¹⁴	6.9	1.5×10^{-4} sec
Polonium, Po ²¹²	8.6	3×10^{-7} sec

* In air at 15°C and 1 atm pressure.

various materials is somewhat dependent upon their atomic weights. A layer of lead 1 mm thick has about the same effectiveness in absorbing beta particles as 5 mm of aluminum. The extent of absorption also varies with the speed of the particles. The slower particles, known as "soft" rays, do not penetrate as deeply as the fast-moving particles, which are sometimes described as "hard" beta radiation.

Gamma rays are short-wave radiations which are not deflected by a magnetic field. They are identical to X rays except that their wavelength is much shorter. These rays have no mass and, consequently, are not thought of as particles. Instead they may be described as a form of electromagnetic radiation similar to light. As a result of their very short wavelength, gamma radiations have the power of penetrating very deeply into solid materials. Their penetration is much greater than that of X rays, and because of this behavior they are known as hard rays. Gamma radiation may penetrate 25 cm of iron and up to 8 cm of lead. Heavy elements, atom for atom, are much more effective as absorbers of gamma radiation than are light elements. Thus lead is about eight times more effective than aluminum and about four times better than copper.

Gamma radiation is believed to arise from transitions between energy levels in the nuclei of atoms. These radiations are somewhat analogous to those making up line spectra, which arise from transitions between the energy levels of the extranuclear structure. Furthermore gamma rays emitted from a given isotope have either the same energies or a discrete set of energies, indicating that nuclear energy levels are probably quantized as are atomic energy levels. Therefore gamma rays can be considered as a nuclear spectrum which may provide information regarding nuclear energy levels in much the same manner as optical and X-ray spectra give knowledge concerning electronic energy levels.

§3 The Disintegration Theory. The discovery of radioactivity stimulated a considerable amount of research on radioactive materials in the early part of the present century. In the course of some of these investigations it was found that uranium, thorium, and radium give rise to a number of other radioactive elements which have a more or less transitory existence. To explain the source of these elements as well as radioactive emanations, Rutherford and Soddy in 1902 advanced their theory of radioactive disintegration. According to this theory radioactive elements undergo spontaneous transformations from one chemical atom into another, and radioactive radiations are emitted in the process. In their writings they made the following statements: "The position is thus reached that radioactivity is at once an atomic phenomenon and the accompaniment of a chemical change in which new kinds of matter is produced. The two considerations force us to the conclusion that radioactivity is a manifestation of subatomic chemical change."

This theory was revolutionary at the time it was put forward because scientists had always regarded elements as being changeless in character. It should be remembered that the disintegration theory was proposed before the idea of a nuclear atom had been developed. In view of present-day knowledge the theory can be understood and explained more adequately than at the time it was first advanced.

The very heavy elements are all radioactive, and the atoms of these elements are unstable. The source of this instability is in the nucleus, which breaks down with the emission of either a helium nucleus (alpha particle) or an electron (beta particle). The disintegration process is not simultaneous but is a series of successive ejections in which the nature of the ejected particle depends on the sequence of the particular disintegration series. A partial chain of such transformations is indicated in the following example:



If it were possible to start with a pure radioactive species, such as radium, it should be obvious that after a period of time the decay series, which

involves an enormous number of atoms, would result in a mixture of atomic species, as, for example, radium, polonium, lead, and bismuth. Some of these atoms would be emitting alpha rays and others beta rays; consequently any radioactive material will emit a mixture of alpha, beta, and gamma rays.

Since radioactive disintegration is a process in certain elements by which one chemical element is transformed into another, it is to be expected that there should be a direct relationship between the loss of a particle and the type of element that is produced. Disintegration reactions may proceed in one of two ways:

1. When an alpha particle is emitted, the atomic weight of the resulting nucleus is decreased by four units and the nuclear charge by two units. These changes result from the fact that the alpha particle has an atomic mass of four units and a nuclear charge of two. The decay product is consequently displaced two groups to the left in the Mendeleev periodic table. If an alpha particle is ejected from a radium atom, the process may be indicated by the equation

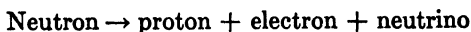


Inasmuch as the ejected alpha particle bears a double positive charge, the resulting radon particle will be in the form of a doubly charged negative ion. However, ionic charges in nuclear transformations have little or no significance. The alpha particles will pick up two electrons from the air and will be converted into helium atoms, whereas the nuclear ionic particles will eventually give up two electrons to surrounding matter. It is of interest that if a nuclear transformation is carried out in a closed vessel the alpha particles will be confined and the vessel will become positively charged over a period of time.

2. When an electron leaves a nucleus in the form of beta emission, there is no appreciable change in atomic weight but the positive charge on the resulting nucleus will be increased by one unit. Therefore the new element will have an atomic number one unit greater than the parent element and will belong to the next group to the right in the periodic table. Such a transformation is postulated by means of the equation



Despite the fact that beta emission has been described as the ejection of an electron by a nucleus, there is ample evidence that an electron cannot exist within a nucleus (Sec. 1·7). It is believed that electrons are produced by the decay of neutrons. The decay may proceed according to the equation



According to this theory of decay the electron escapes as a beta emission, leaving one proton (one positive charge) in the nucleus; consequently the disintegration process increases the atomic number of the nucleus by one unit.

8.4 Rate of Disintegration and Half-life Period. Since the ejection of an alpha or beta particle represents the transformation of one atom of a radioelement into an atom of another element, the activity of a given radioactive element indicates how rapidly it is disappearing. Each radioactive atom is believed to have a tendency to disintegrate. The actual

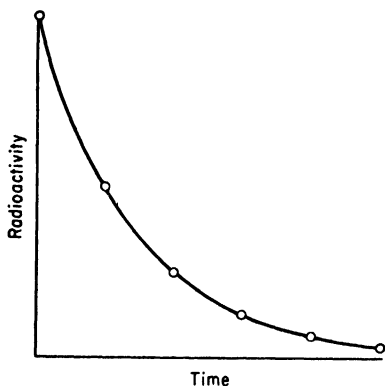


Fig. 8-1 Exponential manner of radioactive decay.

number of atoms of a given material which will disintegrate in a unit of time is proportional to the number of atoms that are present at any time. However, the rate is also dependent upon the characteristic tendency of the atoms of the radioactive element under consideration to disintegrate. Moreover the tendencies (manifested as activities) of the different radioactive elements differ widely. For example, radium atoms have about 3 million times the activity of uranium atoms. A few seconds' exposure of a photographic plate

to the emanations from radium produces a fogging that would require several weeks of exposure to those of uranium. The tendency to disintegrate is manifested as a characteristic factor for each radioelement.

Radioactive decay is a first-order reaction, which means that the activity diminishes in an exponential (logarithmic) manner, as is shown in Fig. 8-1. As disintegrations occur, in a given sample, the number of atoms will diminish and the rate of disintegration must also decrease. If the radioactivity of a radioelement is plotted against time, a logarithmic curve is produced which cuts the axis at infinity. Therefore, in theory, the total decay period of any element is infinity. This being true, any use of total decay periods would be meaningless. It is necessary, however, to make use of some time factor for measuring radioactive decay.

Since the rate of decay decreases with the number of atoms that disappear, it follows that after a definite interval of time a given fraction of the total number of atoms of the radioelement will have disintegrated. If a certain number of atoms in a 1-g sample disintegrate in 1 hr, twice as many atoms will disappear in a 2-g sample and one-half as many will break down in a 0.5-g sample during the same interval of time. (It is con-

venient to fix some decay constant by which the radioactivity of an element may be evaluated or compared with the activities of other radioelements. In 1904 Rutherford introduced such a constant, which he called the *half life* of the radioelement. This is the time required for one-half of any sample to disappear. The half-life period is also a measure of the radioactivity of the element, since the shorter the period of time, the greater is the number of atoms that are disintegrating. As is shown in Table 8.1 the half lives of the radioelements vary widely, ranging from a fraction of a second to millions of years.

The law of radioactive decay may be stated in words to the effect that the quantity of a radioelement which disappears in unit time is directly proportional to the amount present. This law is more significant when expressed mathematically. If the number of atoms that are present at any given instant is denoted as N , then the change in the number of atoms with time is $-dN/dt$. The negative sign shows that N (number of atoms) decreases as t (time) increases. However, the change in number of atoms is proportional to the total number of atoms N ; therefore the mathematical relation is

$$-\frac{dN}{dt} = \lambda N \quad (8.1)$$

where λ is a proportionality constant, which Rutherford and Soddy called the *radioactive constant*, although *decay constant* is probably a better term. Equation (8.1) may be rearranged as

$$\frac{dN}{N} = -\lambda dt \quad (8.2)$$

which may be integrated to give

$$\ln N + C = -\lambda t \quad (8.3)$$

The integration constant C can be evaluated, because when $t = 0$, N has an initial value of N_0 . Therefore, upon substituting for t and N in Eq. (8.3), the result is

$$C = -\ln N_0 \quad (8.4)$$

If the value for the integration constant C is substituted into Eq. (8.4), the resulting equation is

$$\ln N - \ln N_0 = -\lambda t \quad (8.5)$$

When Eq. (8.5) is put into its equivalent exponential form, it becomes

$$\frac{N}{N_0} = e^{-\lambda t} \quad \text{or} \quad N = N_0 e^{-\lambda t} \quad (8.6)$$

The half life of a radioelement may be defined as the time required for a

348 Fundamental Concepts of Inorganic Chemistry

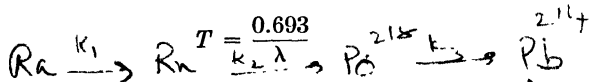
given amount of the element to decay to one-half its initial value. This time is usually represented by T , and it may be evaluated from Eq. (8·6). At the end of one half-life period T the ratio of N to N_0 is one-half. When these values are substituted into Eq. (8·6), the following equation is obtained:

$$\lambda T = -\ln \frac{1}{2}$$

or

$$\lambda T = \ln 2$$

and since $\ln 2 = 0.693$, the equation may be stated as



Therefore, if the decay constant λ is known, the half life of the radioactive element may be evaluated in specific numerical terms.

When a radioactive material stands over a long period of time, a condition known as radioactive equilibrium¹ is established. This equilibrium results from the fact that there is a series of radioactive substances formed successively from a long-lived parent and, after a sufficient length of time, each element in the decay series is formed at the same rate as that of its decay. The general principle underlying the formation of a radioactive equilibrium may be illustrated by using radium and its descendants. It so happens that radium is a fairly long-lived element and will disintegrate into radon at a rate which is practically constant over a period of several months. The radon atoms, in turn, will start disintegrating into Po^{218} , and polonium will begin to disintegrate into Pb^{214} , each at a rate that is proportional to the number of atoms present and their tendency to disintegrate. Eventually the rate at which all the descendants of radium are disintegrating will become equal to the rate at which they are being formed. Under equilibrium conditions the amounts of the radioactive materials will remain constant, because the rate of formation and decay for each particular element will be the same. The amounts of each element present will be inversely proportional to its characteristic tendency to decay. This tendency is usually called the element's decay constant. If the decay constants of the members of a series such as radium, radon, polonium, and lead are λ_1 , λ_2 , λ_3 , and λ_4 , the number of atoms of each member of the series present at equilibrium will be

$$\lambda N_1 = \lambda N_2 = \lambda N_3 = \lambda N_4$$

Moreover, for any two members A and B in the series, regardless of their positions within the series, the following mathematical relationship holds true:

$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \text{constant}$$

¹ Radioactive equilibrium is established only when there is a radioactive series.

8.5 Naturally Occurring Radioactive Elements. Over 700 radioactive isotopes are known at present, and since the number is still increasing, any exact count is impossible. Of this number approximately 50 radioisotopes occur in natural sources, and most of these have high nuclear charges and mass numbers. All naturally occurring elements with atomic numbers greater than 83 (bismuth) are radioactive, and there are in addition several isotopes of thallium, lead, and bismuth that are radioactive. These 40-odd isotopes will be discussed in the next section.

Very few natural radioelements with low atomic numbers are known, and the majority of these are characterized by long half lives and feeble radioactivities. It is quite possible that as detecting instruments are developed with greater sensitivities a few other isotopes which are now considered as stable will be added to this list. The properties of the known natural radioactivities, other than the three radioactive families (Sec. 8.6) are listed in Table 8-2. It should be added that there is some doubt as to whether the active isotope of hydrogen should be classified as a natural radioelement.

TABLE 8-2 NATURALLY OCCURRING RADIOACTIVE ISOTOPES NOT BELONGING TO A DISINTEGRATION SERIES

Isotope	Type of decay	Decay product	Half life, years	Isotopic abundance, %	Decay energies, mev
$^1_1\text{H}^3$	β	$^3_2\text{He}^3$	12.5	—	0.018
$^{12}_6\text{C}^{12}$	β	$^{14}_7\text{N}^{14}$	5.7×10^3	—	0.0155
$^{40}_{19}\text{K}^{40}$	β , γ , and K	$^{40}_{20}\text{Ca}^{40}$ and $^{40}_{18}\text{Ar}^{40}$	1.4×10^9	0.012	1.4 (β) 1.5 (γ)
$^{87}_{37}\text{Rb}^{87}$	β , γ	$^{87}_{38}\text{Sr}^{87}$	6×10^{10}	27.85	0.3 (β) ? (γ)
$^{115}_{49}\text{In}^{115}$	β	$^{115}_{50}\text{Sn}^{115}$	6×10^{14}	95.84	0.63
$^{150}_{60}\text{Nd}^{150}$	β	—	2×10^{10}	5.60	?
$^{152}_{62}\text{Sm}^{152}$	α	$^{148}_{60}\text{Nd}^{148}$	2.5×10^{11}	26.90	?
$^{176}_{71}\text{Lu}^{176}$	β , γ , and K	$^{176}_{72}\text{Hf}^{176}$ and $^{176}_{70}\text{Yb}^{176}$	7.2×10^{10}	2.5	0.4 (β) 0.27 (γ)
$^{187}_{75}\text{Re}^{187}$	β	$^{187}_{76}\text{Os}^{187}$	4×10^{12}	62.93	0.043

Of interest in connection with the activities of the lighter isotopes¹ is the fact that only the samarium radioactivity is one of alpha decay. As our knowledge of nuclear structure grows, it is possible that the mode of decay which characterizes these elements will be better understood. It will be noticed that another type of decay, designated as K , is listed for the isotopes of K and Lu . The symbol K denotes the capture of an orbital electron by the nucleus. Since the electron which is captured

¹ Those isotopes which are lighter in weight and which have smaller atomic numbers than bismuth.

invariably comes from the shell nearest the nucleus, which is the *K* shell, the process is usually called *K*-electron capture. After *K* capture there is a vacancy in an inner orbital, and an electron from a higher energy level moves inward to the *K* shell to fill this vacancy. As will be recalled from Chap. 2, the transition of an electron to the innermost level gives rise to spectral lines in the X-ray region. Consequently *K* capture produces X radiation, and these X rays usually include the entire X-ray spectrum of the daughter element although the *K* lines are the most prominent ones. *K* capture was not included in Sec. 8-2 in our discussion of radioactive emanations, since this type of decay is quite unusual among natural radioelements. However, it does occur quite frequently among synthetic radioisotopes, and we shall mention *K* capture again in connection with artificial radioactivity.

8-6 Radioactive Disintegration Series. Most of the natural radioelements of higher atomic numbers exist in nature as a number of radioactive isotopes. All the 40 or more known species belong to one of three definite chains of successive decays. These chains constitute the three radioactive families, which are known as the *uranium*, *thorium*, and *actinium series*.

The three radioactive families have been named after a prominent member in each decay series. The uranium and thorium series were named for the longest-lived members of their decay series, with half lives of 4.498×10^9 and 1.39×10^{10} years, respectively. The parents of these elements are postulated as having comparatively short lives since they no longer exist in nature. The actinium series was at one time thought to originate with this element, but it has since been discovered that the true parent to the series is a much longer-lived element, U^{235} , which is an isotopic species of uranium with a half life of 7.07×10^8 years. The three families are sometimes referred to as the $4n$ (thorium), the $4n + 2$ (uranium), and the $4n + 3$ (actinium) series, inasmuch as the mass numbers of the members are divisible either by 4, or by 4 with remainders of 2 and 3.

The general characteristics of the three disintegration series are given in Tables 8-3 to 8-5. There is a fairly close similarity among the three series and their modes of decay. Originally, the members of a decay series were designated by names such as uranium I, uranium X_1 , uranium X_2 , etc., and thorium, mesothorium I, etc. These historical names are rapidly becoming obsolete, and we shall refer to the radioisotopes in terms of the element to which each belongs. It is of interest that the ultimate product in each of the three families is a stable, but different in each case, isotope of lead. We have listed the mass numbers of the lead isotopes of the uranium, thorium, and actinium series as Pb^{206} , Pb^{208} , and Pb^{207} , respectively, although the actual masses of the lead isotopes have been

352 Fundamental Concepts of Inorganic Chemistry

series, they are not specifically related. In other words, an isotope in one series will not decay to a particular isotope belonging to another series. This lack of interchange is to be expected, since mass changes can take place only by the loss of alpha particles of four mass units each, and the

TABLE 8-4 THE THORIUM SERIES OF RADIOACTIVE ELEMENTS

Radioactive element	Isotope	Radiation	Half life
Thorium ↓	Th ²³²	α	1.39 × 10 ¹⁰ years
Radium ↓	Ra ²²⁸	β	6.7 years
Actinium ↓	Ac ²²⁸	β	6.13 hr
Thorium ↓	Th ²³²	α	1 90 years
Radium ↓	Ra ²²⁴	α	3.64 days
Radon ↓	Rn ²²⁰	α	54.5 sec
Polonium ↙ ~100% ↘ ~0.014%	Po ²¹⁶	α and β	0.16 sec
Lead	Pb ²¹²	β	10 6 hr
Astatine	At ²¹⁶	α	54 sec
Bismuth	Bi ²¹²	α and β	60.5 sec
Polonium ↙ 66.3% ↘ 33.7%	Po ²¹²	α	3 × 10 ⁻⁷ sec
Thallium	Tl ²⁰⁸	β	3.1 min
Lead	Pb ²⁰⁸	Stable	

characteristic mass of each family is either $4n$, $4n + 2$, or $4n + 3$. On the other hand a radioactive decay chain is not always straightforward, as is indicated by branched disintegrations which occur in each series. In such cases an isotope breaks down in two distinct ways, giving rise to what are called *branched products*. A good illustration of branched disintegration occurs in the thorium series for the isotope of bismuth with a mass number of 212, which breaks down to give two products, one by alpha emission and the other by beta emission. By emitting alpha particles, 33.7 per cent of Bi²¹² is converted into Tl²⁰⁸, and by emitting beta particles the other 66.3 per cent is transformed into Po²¹². It is sig-

nificant that the half life of Bi^{212} is the same irrespective of the end product. It is also true that the isotopes produced by a branched disintegration always decay into the same product. Thus both Tl^{208} and Po^{212} break down into the same isotope, namely, Pb^{208} .

TABLE 8-5 THE ACTINIUM SERIES OF RADIOACTIVE ELEMENTS

Radioactive element	Isotope	Radiation	Half life
Uranium ↓	U^{235}	α	7.07×10^8 years
Thorium ↓	Th^{231}	β	24 6 hr
Protactinium ↓	Pa^{231}	α	3.2×10^4 years
Actinium ↓	Ac^{227}	α and β	21.7 years
99.8% ↓ 1.2% ↓ Thorium ↓ Francium ↓	Th^{227} Fr^{223}	α β	18.9 days 21 min
Radium ↓	Ra^{223}	α	11.2 days
Radon ↓	Rn^{219}	α	3 92 sec
Polonium ↓	Po^{215}	α	1.82×10^{-3} sec
Lead ↓	Pb^{211}	β	3.61 min
Bismuth ↓	Bi^{211}	α and β	2 16 min
99.98% ↓ 0.02% ↓ Polonium ↓ Thallium ↓	Po^{211} Tl^{207}	α β	5×10^{-3} sec 4 76 min
Lead	Pb^{207}	Stable	

8.7 ✓ The Neptunium Disintegration Series. It has been stated that the three series of natural radioelements contain members whose masses are divisible by 4, or by 4 with remainders of 2 and 3. For many years scientists speculated upon the failure to find a disintegration series in nature whose isotopic masses carry a numerical relationship of $4n + 1$. At least two scientists went so far as to work out a hypothetical decay scheme for such a series. The most plausible explanation for the absence of this series in nature was that no member of the scheme was sufficiently

354 Fundamental Concepts of Inorganic Chemistry

long-lived to have survived over the years since the series might have been formed. The first five members of this series were discovered at Berkeley, Calif., during the course of the World War II atomic-energy

TABLE 8-6 THE NEPTUNIUM SERIES OF RADIOACTIVE ELEMENTS

Radioactive element	Isotope	Radiation	Half life
Plutonium ↓	Pu ²⁴¹	β	13 years
Americium ↓	Am ²⁴¹	α	470 years
Neptunium ↓	Np ²³⁷	α	2.20 × 10 ⁶ years
Protactinium ↓	Pa ²³³	β	27.4 days
Uranium ↓	U ²³³	α	1.62 × 10 ⁵ years
Thorium ↓	Th ²²⁹	α	7.34 × 10 ⁴ years
Radium ↓	Ra ²²⁶	β	14.8 days
Actinium ↓	Ac ²²⁶	α	10.0 days
Francium ↓	Fr ²²¹	α	4.8 min
Astatine ↓	At ²¹⁷	α	0.02 sec
Bismuth ↙ 98% ↘ Polonium Thallium	Bi ²¹³	α and β	47 min
	Po ²¹³ Tl ²⁰⁹	α β	4.2 × 10 ⁻⁶ sec 2.2 min
Lead ↓ Bismuth	Pb ²⁰⁹ Bi ²⁰⁹	β Stable	3.3 hr

project. The other members have been discovered and studied independently as the result of the development of interest in the series during the wartime project.

The neptunium series derives its name from the longest-lived member of the group, neptunium, whose half life has been calculated to be 2.20×10^6 years. This series differs in several respects from the naturally occurring radioactive series. These differences are condensed into the following items:

1. The end product in the series is the stable isotope of bismuth, $_{83}\text{Bi}^{209}$,

whereas the end products of the three natural radioactive series are stable isotopes of lead.

2. The only member of the series to be found in nature is the stable end product, bismuth, $_{83}\text{Bi}^{209}$.

3. The series contains no gaseous emanations as do the three natural series.

4. The series contains isotopes of francium and astatine as direct and successive members of the decay chain. These elements appear only as minor branched disintegration products in the natural series.

5. Branched disintegration appears to be of more frequent occurrence in the naturally radioactive series than in the neptunium series.

TABLE 8-7 ESTIMATED AGE OF THE EARTH AND HALF LIVES OF LONG-LIVED ISOTOPES

Series	Longest-lived isotope	Half life, millions of years
$4n$	$_{90}\text{Th}^{232}$	13,000
$4n + 1$	$_{93}\text{Np}^{237}$	2.2
$4n + 2$	$_{92}\text{U}^{238}$	4,500
$4n + 3$	$_{92}\text{U}^{235}$	707
	Age of earth	2,000-3,000

We have inserted the neptunium disintegration series at this point for convenience of study and comparison. Since the members of the series are man-made, or artificial, radioelements, we shall have occasion to mention the series and its members again in our discussion of artificial radioactivity.

8-8 The Age of the Earth. The existence of considerable amounts of the radioactive substances uranium and thorium in nature, and the absence of neptunium, provide some basis for an estimate of the age of the earth. This statement is made on the assumption that the genesis of these radioelements was in the same geologic period as other elements. Inasmuch as the disintegration of uranium and thorium releases helium and results in an end product of certain isotopes of lead, it is possible by chemical analyses to determine the ratio of uranium or thorium to helium or lead and thereby to estimate the period of time since the formation of the parent element (Sec. 8-4).

Thorium occurs in larger quantities within the earth's crust than does uranium. The half life of the longest-lived isotope of thorium, Th^{232} , is 13,000 million years; consequently it may be assumed that the age of the earth is much less than this figure. The half life of the longest-lived isotope of uranium, U^{238} , is 4,500 million years. The minerals containing this element are in less quantities than those of thorium. The half life of

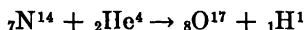
356 Fundamental Concepts of Inorganic Chemistry

the uranium isotope, U^{235} , which is the precursor of the actinium series, is 707 million years, and this element occurs in a very small percentage within the earth's crust. On the other hand the longest-lived isotope of neptunium has a half life of 2.2 million years, and this element has not been found in nature. From these values and the chemical analyses of the decay products of thorium and uranium the age of the earth has been estimated to be between 2,000 and 3,000 million years. In Table 8-7 are listed the half-life periods of the longest-lived members of the four disintegration series and the approximate age of the earth.

4.5 billion years

NUCLEAR TRANSFORMATIONS AND ARTIFICIAL RADIOACTIVITY

The first artificial nuclear transmutation to be recognized and described as such was reported by Rutherford in 1919. He observed that when high-speed alpha particles from radium C', Po^{214} , were passed through nitrogen gas, scintillations were produced upon a zinc screen even when sufficient material was placed between the nitrogen and the screen to absorb all alpha particles. The long-range particles causing the scintillations were identified as protons by means of their deflection in a magnetic field. The results of this experiment were correctly interpreted by Rutherford as a nuclear reaction between nitrogen atoms and alpha particles to give oxygen atoms and protons. The nuclear equation for the transformation is



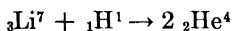
Similar disintegrations were observed by Rutherford and Chadwick between 1920 and 1924 for all the elements between boron and potassium on the atomic-weight scale, except carbon and oxygen. At first there was some doubt as to whether the proton was produced by the impact of the collision between the nucleus and alpha particle or whether the alpha particle entered the nucleus and caused the ejection of the proton. In 1923 P. M. S. Blackett obtained cloud-chamber photographs showing that the alpha particle actually disappeared in the disintegrating collision. These were the first noteworthy experiments in nuclear transformations.

The use of alpha particles from radioactive nuclei as projectiles to effect transmutations was hampered by several limitations. These particles arise from their radioactive source in all directions and cannot be focused upon target material; consequently the efficiency of the transmutation is quite low. Also, both the alpha particles and the nuclei of the target atoms are positively charged, and the forces of repulsion between these particles must be overcome before transmutation is possible. The repulsive forces are usually referred to as a *potential barrier*. Because of this potential barrier, natural alpha particles do not have sufficient energies to

penetrate the nuclei of heavy elements. It should be remembered that the heavier the element the greater is its nuclear charge.

8-9 Methods for Producing Nuclear Projectiles. Up to 1932, alpha particles from radioactive sources were the only known projectiles with sufficient energies to produce nuclear transmutations, and even these projectiles were ineffective for the disintegration of heavier nuclei. For a considerable time it was recognized that the singly charged proton, ${}_1\text{H}^1$, would be a much more effective nuclear projectile, but it was not available as a high-speed particle from radioactive materials. These facts stimulated a search for means of accelerating various particles which might be used as nuclear projectiles. The first production of high-speed protons with sufficient energies to cause nuclear transformations was achieved by Cockroft and Walton in Rutherford's laboratory in 1932 by means of high-energy discharge tubes. In the meantime an even more important instrument, designated as a *cyclotron*, was conceived and built by E. O. Lawrence and coworkers at the University of California to accelerate various types of positively charged particles.

The device built by Cockroft and Walton was a form of electrostatic accelerator in which protons, produced by ionization of hydrogen in an electric discharge, were admitted through slits to an accelerating tube. There, by means of a cascade arrangement, the protons were accelerated by a potential difference of 200,000 volts before being directed upon a target. Cockroft and Walton observed that high-speed protons striking a target of mica containing a lithium salt caused a disintegration of lithium atoms into alpha particles. The nuclear equation for the reaction is



Not only was this the first truly artificial transmutation to be produced, but it was the first case of an artificial thermonuclear reaction. Although not recognized at the time, the bombarding protons had much less energies than the energies of the resulting alpha particles. The topic of thermonuclear reactions will be discussed later (Sec. 8-11), but it may be said that in this particular nuclear reaction the bombarding proton simply serves as a trigger to release a tremendously large quantity of exothermic energy.

Of all the instruments which have been devised for accelerating nuclear projectiles the one which has attracted the widest interest is the cyclotron of E. O. Lawrence. Instead of producing high voltages directly as in the voltage accelerator of Cockroft and Walton, the positively charged particles (protons, deuterons, or alpha particles) are accelerated by passing them more than 100 times each through a large difference in potential. The cyclotron consists of two large hollow semicircular electrodes shaped

like capital D's, commonly called *dees*, which are separated from one another by a narrow gap. These dees reside in a closed vessel, containing hydrogen, deuterium, or helium gas at low pressure, placed between the poles of a powerful magnet, P_1 and P_2 . A high-frequency alternating potential is applied between the dees so that a given dee is positive one moment and negative the next. At F , near the center of the system, and between the two dees, is an electrically heated filament which by emitting

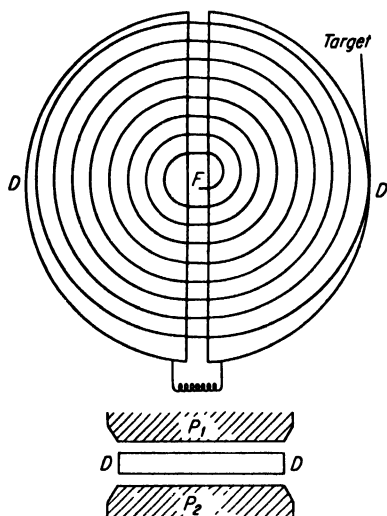


Fig. 8-2 A schematic representation of a cyclotron with two dees.

electrons produces ionization in the surrounding gas. Consequently F can be considered as the source of the positive ions which are used as projectiles. Figure 8-2 is a schematic representation of a cyclotron with its two dees.

A positive ion originating from source F will be attracted to the dee of opposite charge. Once within the dee the speed of the ion remains constant, and its pathway is semicircular because of the influence of the magnetic field. After completing the semicircle in a given dee the ion reaches the gap between the dees, where it is acted upon by the difference in applied potential. If the oscillating frequency of the current synchronizes with the time

necessary for the particle to pass through its semicircular path, the sign of the potential will have been reversed, so that the ion is now attracted across the gap to the other dee. In passing across the gap the ion gains additional speed because of the potential difference between the two dees. Within the second dee the particle is moving faster; consequently its circular path, produced by the influence of the magnetic field, will have a greater radius than in the first dee. This process is repeated 100 times or more. With each passage across the gap the speed of the particle increases. In like manner the radius of the path described by the ion will increase until eventually it reaches the outer circumference of the dee, where it is diverted from its circular path by a negatively charged plate and directed upon its target.

The maximum velocity which may be acquired by a particle is determined by the field strength of the magnet and the diameter of the dees. The first practical cyclotron built by Lawrence had a magnet with pole

faces 11 in. in diameter which yielded protons with energies of 1.22 Mev. The 184-in. cyclotron at Berkeley produced particles with energies of about 400 Mev. There is a limit to the energy which may be imparted to ions through acceleration in the original type of cyclotron. The theory of relativity predicts, and experimental evidence confirms, that, as the velocity of a particle approaches the velocity of light, its mass increases. In a very large cyclotron the mass of an ionized particle increases as it moves toward the outer edge of the dee; consequently the enlarged mass will augment the time necessary for the ion to pass through its semi-circular path. This lag in time for the last passageways results in the particle arriving at the gap too late for the change in frequency of the current. In other words, the frequency of the current will no longer be synchronized with the time for the particle to pass through its semicircular path.

To compensate for the relativistic increase of mass with velocity, frequency modulation is now used to keep the alternating potential in phase with the passage time of the accelerating particle. This modified cyclotron, called a *synchrocyclotron*, employs only one dee, and the particles are alternately pulled into and pushed out of the dee as they follow circular paths between the poles of the magnet.

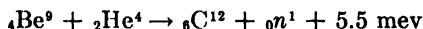
A more recent accelerating instrument, called the *synchrotron* and nicknamed the Bevatron because of the magnitude of the energies imparted to the accelerated particles, has been built at the University of California at Berkeley. This accelerator is capable of accelerations above 1 Bev. It employs modulation of both the electric accelerating field and the magnetic focusing field. The machine is designed to produce 10-Bev protons, and it is with particles of such energies that it has been possible to produce antiprotons (Sec. 1-3).

The discovery of the neutron by Chadwick (Sec. 1-4) in 1932 added another projectile for use in nuclear transformations. This particle, being electrically neutral, is not subjected to electrostatic repulsion, as are positively charged particles, when nearing a nuclear target. Consequently it can penetrate quite easily into an atomic nucleus, and it does not have to be moving rapidly in order to effect transmutation. In fact slow neutrons are usually more effective than fast ones, inasmuch as rapidly moving neutrons may pass through a nucleus without causing transmutation. It might also be added that the fact that the neutron bears no charge prevents acceleration of the particle by any of the accelerating devices that are used for charged particles. Although neutrons are the most effective and versatile of projectiles for ordinary use, they suffer the objection that they themselves must be produced by nuclear reactions.

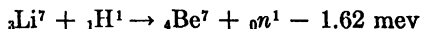
The bombardment of beryllium with alpha particles produces high-

360 Fundamental Concepts of Inorganic Chemistry

speed neutrons. The high velocity of the neutrons is a consequence of the energy of the reaction.



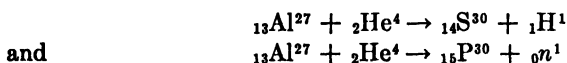
The magnitude of the reaction energy is a qualitative indication of the velocity of a resulting nuclear particle. For example, slow neutrons may be expected from bombarding lithium with protons, since the reaction energy is a negative value.



However, in this case the energy of the reaction is somewhat dependent upon the energies of the protons used as projectiles.

8-10 Artificial Radioactivity. Of the hundreds of isotopes that are known, the majority are man-made, and most of these are unstable. When nuclei are bombarded with high-velocity projectiles, the resulting products are frequently radioactive. They are found to disintegrate during a period of time which is characteristic for each product. The radioactivity produced by bombardment in atomic transmutations is called *induced*, or *artificial, radioactivity* to distinguish it from natural radioactivity. Usually the decay which takes place in man-made isotopes is a single process, although there are cases where the disintegration follows a pattern similar to that in the natural radioactive series. The members of the neptunium series may be considered as species of artificial radioactivity, and as such they possess properties quite similar to the members of the natural radioactive series.

Artificial radioactivity was first discovered by Irène Curie-Joliot and her husband F. Joliot in 1934. The Joliot's bombarded boron and aluminum with alpha particles from polonium and obtained the emission of positrons, protons, and neutrons. It was observed that the emission of positrons increased during the bombardment to a limiting value. However, when the bombardment was stopped, the emission of protons and neutrons ceased but that of positrons did not. The emission of positrons continued but decreased exponentially with time in a manner similar to radioactivity in a natural radioisotope. Apparently during bombardment two nuclear reactions were taking place. In the case of aluminum the equations for the two reactions may be written as



The emission of positrons may be attributed to the radioactive isotope of phosphorus, which decays according to the equation



The discovery of artificial radioactivity has opened up wide fields of research. By means of isotopic tracers it is possible to follow the course of various chemical reactions that have hitherto been obscure. These tracers also permit investigations of metabolic processes in living cells and tissues, and sometimes they may be used for treatment of unbalanced metabolic conditions. Isotopic tracers are of commercial importance in various metallurgical industries for studying the properties of metals and alloys. The possible uses of isotopic tracers seem almost unlimited, and such uses have already developed into a broad field in itself. It should also be mentioned that artificial radioactivity seems likely to provide the key to the conversion of thorium into a relatively cheap atomic fuel.

In Sec. 8-2 the products of natural radioactive decay were listed and described as alpha, beta, and gamma radiation. In addition to the processes taking place in natural radioactive materials by which these radiations are produced, there are two other modes of decay which may characterize artificial radioactivity. These additional decay processes are designated as *positron emission* and *orbital-electron capture*. As implied by their descriptive names, the first mode of decay results in the emission of positrons (Sec. 1-3), whereas the second involves the capture of electrons.

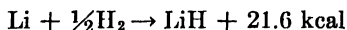
The positron has the physical characteristics of a positive electron. Although it is a stable particle, it does not survive for long because of interaction with electrons, which are present in all materials. Positrons are believed to result from transformations of protons into neutrons within the nucleus. The emission of a positron decreases the nuclear charge by one unit but has no effect on the mass number. In Sec. 1-8 the Yukawa theory was explained, concerning possible interactions within the nucleus. From reactions between neutrons and protons it is possible to produce the emission of either electrons or positrons. To carry this theory a little further, it seems possible to make a qualitative prediction as to which particle will be emitted. In general, if the radioactive isotope has a smaller proton:neutron ratio in its nucleus than has the corresponding stable isotope, then the particle emitted will be an electron, inasmuch as this emission will increase the foregoing ratio. On the other hand, if the proton:neutron ratio is higher than that in the stable isotope, the emitted particle will be a positron. Such behavior is characteristic among man-made light isotopes. Apparently the margin of stability is governed very closely in the lighter elements by the proton:neutron ratio.

Orbital-electron capture was mentioned in Sec. 8-5 in connection with natural radioisotopes which do not belong to the three decay series. *K* capture, as it is called, is a mode of decay in which the nucleus of an element captures an electron from its *K* shell (1s energy level). Because

362 Fundamental Concepts of Inorganic Chemistry

of the vacancy so created, another electron from a higher energy level will drop to the *K* shell to replace the captured one. As the latter electron falls from a higher to a lower level, energy is released in the form of radiation. The wavelength of the radiation produced by such a transition is always in the X-ray region and is characteristic of the product-element.

✓ **8-11 The Energetics of Nuclear Reactions.** Ordinary chemical reactions involve interactions between whole atoms in which energy changes are involved. The usual chemical unit for energy changes is the kilocalorie, and a chemical equation may be classified as endothermic or exothermic on the basis of whether energy is absorbed or released in the course of the reaction. For example, metallic lithium may react with hydrogen to release 21.6 kcal of energy in forming one mole of lithium hydride. The equation is



The energy unit is expressed in kilocalories per *mole*, and since 23.05 kcal is equivalent to 1 *ev*/mole, the reaction indicated by the foregoing equation is one involving an energy change of slightly less than 1 *ev*/mole of lithium hydride formed.

Nuclear reactions involve interactions between nucleons in which there are also energy changes; however, the values of these energy changes are of an entirely different magnitude and are usually many millions times those of chemical reactions. For example, the experiment of Cockroft and Walton (Sec. 8-9) of bombarding a lithium salt with high-speed protons released tremendous energy as the lithium nucleus and proton were converted into two helium nuclei. The source of this energy is the conversion of a certain quantity of mass into energy. Einstein's theory of the equivalence of mass and energy postulated a fundamental relationship that can be expressed by the equation (Sec. 1-10),

$$E = mc^2$$

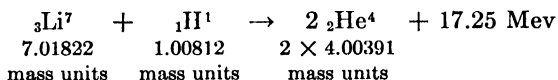
in which *E* is the total energy released, *m* is the mass, and *c* is the velocity of light (10^{10} cm/sec). Consequently any nuclear equation must be balanced in terms of both mass and energy. The relationship may be indicated as

$$\text{Mass}_1 + \text{energy}_1 = \text{mass}_2 + \text{energy}_2$$

In their experiment Cockroft and Walton determined the total energy released through the bombardment of lithium with protons by measuring the range of the alpha particles which were emitted. After subtracting the energy of the incident proton (the energy of the lithium nucleus is

negligible), each alpha particle had an energy value of 8.62 Mev, or a total of 17.25 Mev.

The over-all energy released or absorbed in a nuclear reaction is called the *nuclear reaction energy* and is usually designated as the Q of the reaction. The quantity Q may be either negative or positive. A positive Q denotes that energy is released, and such a reaction is said to be *exoergic*, whereas a negative Q indicates the absorption of energy and the process is designated as *endoergic*. The reaction between the lithium nucleus and a proton is an exoergic process, and Q is positive. This exoergic energy comes from the disappearance of a given quantity of mass; consequently the 17.25 Mev of energy released must be equivalent to the amount of mass lost in the nuclear process. In writing a *complete* equation for a nuclear process it is necessary to show the total masses involved as well as the over-all energy change. Such an equation would appear as



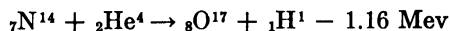
In terms of mass and energy the equation may be written as

$$8.02634 \text{ mass units} = 8.00782 \text{ mass units} + 17.25 \text{ Mev}$$

Therefore $17.25 \text{ Mev} = 8.02634 - 8.00782 = 0.01852 \text{ mass unit}$

From numerous nuclear processes it has been established that one mass unit is equivalent to 931 Mev. Therefore, if the total mass lost or gained in a nuclear reaction is known, the energy value can be evaluated by multiplying by 931 Mev, or, conversely, if the energy value is known, the amount of mass that is converted in the process may be determined by dividing by 931 Mev. In comparing chemical reactions with nuclear processes we should point out the fact that energies of chemical reactions are expressed in *kilocalories per mole*, whereas, in nuclear processes, energy values are denoted in *millions of electron volts per individual nucleus*.

Another aspect to be considered in the discussion of energetics in nuclear processes is the energy requirement of a positively charged projectile in overcoming the potential barrier of a nucleus. This energy value does not appear in a nuclear equation, but nevertheless it may determine whether a nuclear reaction can take place or not. For example, in Rutherford's famous experiment of bombarding nitrogen nuclei with alpha particles to produce oxygen nuclei, the Q for the reaction is a negative value.



The negative value of -1.16 mev might indicate that alpha particles with kinetic energies of this value could bring about the nuclear reaction.

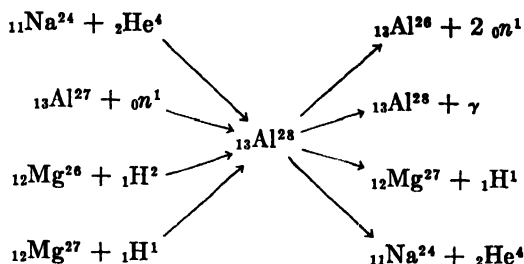
However, such a conclusion would be erroneous, inasmuch as the particles must penetrate the potential barrier (repulsive force) of the nitrogen nuclei, and the requirements for the penetration by alpha particles is greater than indicated by the Q of the reaction. Actually the kinetic energy of an alpha particle must be approximately 3.4 Mev to penetrate the potential barrier of the nitrogen nucleus. The alpha particles of Rutherford's experiment were derived from Po^{214} and possessed kinetic energies of approximately 7.6 Mev. Therefore the Q value of a nuclear reaction may indicate the amount of energy released or absorbed, but it does not show the energy requirement of the positively charged projectile in overcoming the potential barrier of the nucleus which is being bombarded. It now becomes clear why Rutherford and Chadwick were able to secure disintegrations among light elements with alpha particles, but not for the heavier elements. The nuclear charges on heavy atoms are so large that only greatly accelerated alpha particles, of the order of 20 to 30 Mev, can penetrate the potential barriers of these atoms.

8-12 The Formation and Behavior of a Compound Nucleus. From our discussion of nuclear structure as presented in Chap. 1 we know that the composition of the nucleus is a matter of speculation. However, we do have many reasons for believing that a nucleus is a system of neutrons and protons, densely packed in an orderly manner, which are held together by very strong forces that may be the result of a constant interchange between mass and energy. Furthermore there is some evidence that certain ratios of neutrons to protons affect the stability of a nuclear system. The majority of isotopes occurring in nature have stable nuclei, although a few are unstable, and these are the ones which are radioactive. On the other hand most of the man-made isotopes are unstable and radioactive, indicating that a nuclear rearrangement is in progress through which stability is being sought. It is to be expected, therefore, that the bombardment of stable nuclei by various projectiles may produce a condition of instability.

In 1936 Bohr developed a theory to explain what happens when nuclei are bombarded by particles of moderate energies. Projectiles of this description have kinetic energies up to 40 Mev. According to Bohr's theory the incident particle enters the nucleus to form a metastable structure, termed a *compound nucleus*, the latter having a lifetime of 10^{-14} to 10^{-12} sec. During this interval the additional energy from the projectile is distributed throughout the nucleus. The distribution of energy results in an unstable, or "excited," condition, so that eventually one particular nucleon, or combination of nucleons, acquires sufficient energy to escape, thereby leaving behind a more stable structure. When the energy of a compound nucleus is not sufficient to produce the ejection of

a particle, the excess energy may be emitted in the form of gamma radiation.

The Bohr theory describes the formation and breaking down of a compound nucleus as two separate steps which are independent of each other except as to the energies involved in the two processes. In other words, a compound nucleus may be formed in several different ways and may break down in a variety of fashions, but the processes are unrelated except as to their energy requirements. The two essential steps in the theory may be illustrated by assuming that an isotope of aluminum, ${}_{13}\text{Al}^{28}$, may behave as a compound nucleus. The compound structure could conceivably be formed by bombarding certain isotopes of sodium, magnesium, and aluminum with alpha particles, protons, deuterons, and neutrons. The second step involving the disintegration of the nucleus may also take place in a variety of ways. The formation and decay of the compound nucleus may be indicated by the following series of possible nuclear equations:



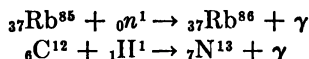
The main feature of the Bohr theory is the fact that, once a compound nucleus has been formed, its subsequent behavior depends not on the mode of formation but on the amount of energy involved. A compound nucleus formed by the entry of a slow (thermal) neutron into the nuclear structure will have a low degree of excitation. Such a structure would probably not eject a nuclear particle in its decay but might instead restore stability by the emission of gamma radiation. On the other hand the penetration of a nucleus by a high-speed alpha particle should produce a compound nucleus with a high degree of excitation, and the resulting product would be expected to emit one or more particles. In recent years considerable progress has been made in predicting the relative probabilities of competing nuclear reactions, especially those reactions produced by projectiles of moderate energies.

8-13 Types of Nuclear Reactions. It is possible to classify nuclear reactions either in terms of the over-all energy transformation that occurs or in terms of the types of projectiles that are used in the bombardments

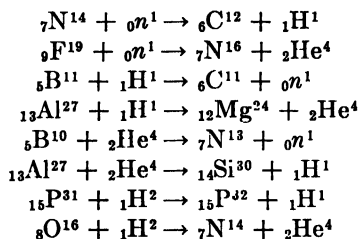
366 Fundamental Concepts of Inorganic Chemistry

of target nuclei. The Bohr theory postulates that the transformation which may occur depends more upon the energy of the projectile than upon its nature. Except for neutron reactions this theory seems to hold true for projectiles of moderate energies. The various transformations which may take place in nuclear reactions can be classified into five types:

1. *Projectile-capture Reactions.* The absorption of slow neutrons is possible for nearly all nuclides. Frequently the neutron capture is followed by gamma emission. It is also possible to have proton capture with gamma emission, but this reaction is common only for target nuclei with low mass numbers. Typical equations for these reactions are



2. *Projectile-capture Particle-emission Reactions.* The majority of nuclear reactions come under this category. The penetration of a nucleus by a projectile is usually followed by the emission of one or more particles as the compound nucleus attempts to attain stability. The nature of the emitted particle, or particles, is largely dependent upon the energy of the projectile. A variety of projectiles and emitted particles are indicated in equations for various sample reactions.

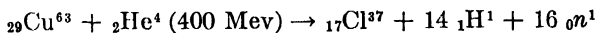


3. *Fission Reactions.* A fission reaction is one in which a heavy nucleus is broken into two or more medium-heavy fragments. The process is usually accompanied by neutron emission, and rarely by other particle ejection. The fission process occurs in nearly all nuclei with mass numbers above 200 when bombarded with neutrons or other projectiles of sufficient energy. A few nuclei undergo fission when bombarded with slow, or thermal, neutrons of little energy. We shall have occasion to discuss the latter reaction in Sec. 8-16. A typical fission reaction is indicated by the equation

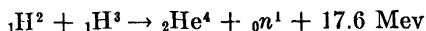


4. *Spallation Reactions.* High-speed projectiles with energies approximating 400 mev may chip fragments from a heavy nucleus, leaving a smaller nucleus which can be identified. Usually the nucleus so pro-

duced has an atomic number between 10 and 20 units lower than the original nucleus. Spallation differs from ordinary nuclear reactions to the extent that in the ordinary type of reaction the nucleus is rarely reduced in atomic number by more than 2. Spallation differs from fission in that the reaction is not self-sustaining. Moreover the change in mass for a spallation reaction is not so great as that in fission. A hypothetical spallation reaction may be indicated by the following equation:



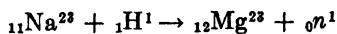
5. *Fusion Reactions.* Isotopes of the very light elements may react with one another to form heavier and more stable nuclei. The potential barriers for reactions of this type are extremely high. Only at very high temperatures, of the order of millions of degrees, may these barriers be overcome. It is believed that the energies of the stars may be derived from reactions of this kind. Fusion reactions are discussed in more detail in Sec. 8-17. A typical fusion reaction takes place between the heavy isotopes of hydrogen, deuterium, and tritium, in which the helium nucleus is the product.



A nuclear fusion reaction is the source of the tremendous energy developed in the detonation of the so-called "hydrogen bomb."

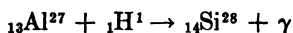
8-14 **Nuclear Reactions Induced by Charged Projectiles.** The penetration of a nuclear structure by a charged particle not only provides additional kinetic energy to the nucleons present but also tends to increase the proton:neutron ratio within the nucleus. Consequently it is not surprising that a compound nucleus so produced may undergo positron emission or orbital-electron capture, as well as the ordinary modes of decay. The majority of charged-particle reactions fall into one of three classifications:

1. *Nuclear Reactions Induced by Protons.* The most important of proton-induced reactions are the (p,n) type. Such reactions are usually endoergic since the exchange of one proton for one neutron involves $1.00893 - 1.00813 = 0.0008$ mass unit; consequently the proton must have not only enough energy to penetrate the potential barrier but also sufficient energy to balance the loss of mass ($0.0008 \times 931 \text{ Mev}$). A typical (p,n) reaction is

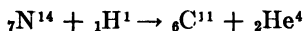


As mentioned in Sec. 8-13, reactions of the (p,γ) type are known but they are largely limited to elements with low mass numbers. An illustrative

equation is



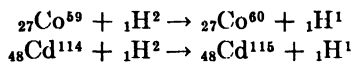
The (p, α) reaction is more common than the (p, γ) type, and this reaction is also largely restricted to nuclides in the low mass region. Such a reaction is



Other proton-induced reactions such as $(p, 2n)$ and $(p, 3n)$ have been observed, but the energy requirements of these reactions are too high for them to be common.

2. Nuclear Reactions Induced by Deuterons. These are the most effective of the charged projectiles. The penetration of a nucleus with ordinary mass number by a deuteron means the addition of approximately 16 Mev of energy to the structure. On the other hand the bonding energy within the deuteron (proton to neutron) is only 2 Mev; hence the fusion of the deuteron with the target nucleus involves a net energy gain of 14 Mev.

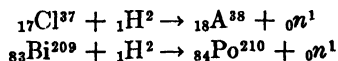
Deuteron reactions are as a whole quite similar to proton reactions. However, the (d, p) reactions are of special interest, because of the ease with which they take place. The energy requirements to produce this type are considerably less than for the (d, n) reactions; yet it would seem that the amount of energy necessary for the deuteron to penetrate the nucleus in both types of reactions should be approximately the same. It is now believed¹ that in a (d, p) reaction the deuteron is polarized as it approaches the nucleus. As the polarized projectile nears the positive nucleus, the repulsive force becomes sufficient to rupture the deuteron, followed by a capture of the neutron and a repulsion of the proton. Thus a (d, p) reaction takes place in two steps: the rupture of the projectile into a neutron and a proton, and then the capture of the resulting neutron. The compound nucleus so produced does not have sufficient energy to eject a particle, but it does lose its energy of excitation by gamma radiation. Although the rejected proton appears to be an emitted particle, it is doubtful if it were ever a part of the compound nucleus as evidenced by the low energy requirements of this type of reaction. Examples of (d, p) reactions are



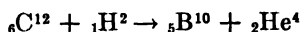
The (d, n) -type reactions are also important. In these reactions the deuteron penetrates the potential barrier of the target element, and from the compound nucleus thus produced a neutron is expelled. Again the

¹ J. R. Oppenheimer and M. Phillips, *Phys. Rev.*, **48**: 500 (1935).

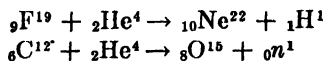
low binding energy between the nucleons within the projectile contributes to the ease with which the (d,n) reaction proceeds. Typical reactions of this type are



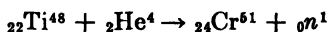
Because of the high potential barrier preventing the escape of alpha particles, reactions of the (d,α) type can be obtained only with high-speed deuterons bombarding target elements of low mass numbers. Such a reaction is



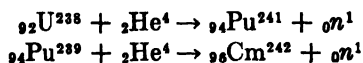
3. *Nuclear Reactions Induced by Alpha Particles.* Rutherford's discovery of transmutation came through an alpha-induced reaction in which nitrogen nuclei were bombarded with alpha particles derived from a radioactive isotope of polonium. The discovery of the neutron by Chadwick was also the result of an alpha-induced reaction in which beryllium was the target element. As we have said before (Sec. 8 9), alpha particles from radioactive sources were the only known projectiles for nuclear bombardment prior to 1932. Consequently alpha particles played a prominent role in the early development of nuclear chemistry. On the other hand the large charge on this projectile causes alpha-induced reactions to be inefficient except for targets with low atomic weights. The high potential barriers of heavy nuclei cannot be penetrated by alpha particles unless these particles have greater kinetic energies than they ordinarily possess when derived from natural radioactive sources. The most important transmutations by alpha particles from natural sources are the (α,p) and (α,n) types. Examples of these are



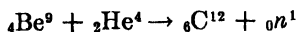
When the kinetic energy of alpha particles is increased by some accelerating device, such as the cyclotron, it is possible to utilize them to produce reactions of the spallation type (Sec. 8·13). Less drastic reactions may be produced by alpha particles with less acceleration, for instance,



Of even greater interest is the fact that the synthesis of certain transuranic elements may be accomplished with high-speed alpha particles. These elements will be discussed more completely in Secs. 8·18 to 8·24. Two such syntheses are

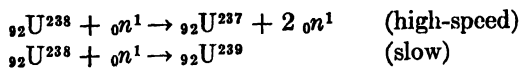


8-15 Nuclear Reactions Induced by Neutrons. The neutron, being a neutral particle, is not subjected to electrostatic repulsion when it approaches an atomic nucleus. Consequently it is the most versatile and the most widely used of atomic projectiles. All elements except helium, ${}_2\text{He}^4$, have been transmuted by neutron bombardment. Neutrons differ from other projectiles in that they can be produced only by nuclear reactions and once produced cannot be accelerated. The most common source of neutrons except a reactor is by the action of alpha particles, produced from radon, upon a beryllium salt. In fact, this is the same target used by Chadwick in his discovery of the neutron.



Because of the short range of alpha particles it is necessary to mix the alpha emitter fairly intimately with the beryllium material. Neutrons in quantity may be produced through a chain-reacting pile in which uranium is undergoing fission (Sec. 8-16).

Neutrons as produced from nuclear reactions are traveling at speeds comparable with the velocities of other bombarding projectiles. The kinetic energies of these particles ordinarily range from 1 to 13 Mev. Usually the product obtained by bombarding a target element with neutrons depends upon the speed of the neutrons. As we have said before, neutrons differ from charged projectiles in that they do not have to overcome a potential barrier in entering a nuclear structure. Accordingly either slow- or fast-moving neutrons may penetrate the nucleus with equal ease. However, the energy of the projectile may determine the course of the reaction. A high-speed neutron may strike a nucleus and apparently pass through it. In other cases the result may be a non-capture disintegration in which a particle is emitted from the nucleus because of the impact. On the other hand a slow neutron may be captured and absorbed by the nucleus. To illustrate these differences, the bombardment of uranium with slow and high-speed neutrons gives rise to two different isotopes of uranium, as is indicated in the following equations:



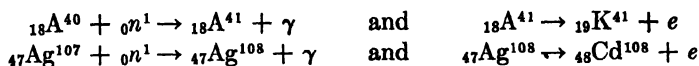
Frequently, slow neutrons are more effective in producing nuclear reactions than are high-speed neutrons. For example, the slower species is more effective in causing fission in ${}_{92}\text{U}^{235}$ than is the more energetic neutron. Slow neutrons are usually termed *thermal* neutrons because they have been slowed down until their kinetic energies are approximately the same as surrounding particles. As may be recalled from

physical chemistry, thermal energies are dependent only upon temperature. Certain materials containing very light elements are used to reduce the speed of neutrons. These materials are termed *moderators*, and they act to decelerate the neutrons by elastic collisions in which there is a minimum of absorption. Water, paraffin, wax, heavy water, and graphite are good moderators and do not enter easily into nuclear reactions with neutrons. Approximately 18 collisions with hydrogen nuclei are necessary to reduce 1-Mev neutrons to thermal energies, and 114 collisions with carbon are necessary to produce the same result. On the other hand hydrogen has a much greater tendency to absorb slow neutrons than carbon and is less desirable in that respect. Deuterium is probably the most effective moderator that is available in practical quantities.

The interaction of a neutron and a nucleus usually gives rise to a compound in which the ratio of mass to charge is too large. Furthermore a neutron contributes approximately 8 Mev as binding energy when it is amalgamated into a nucleus, plus the kinetic energy of the incident particle. Hence it is to be expected that the compound nucleus, being in an excited state, will attempt to secure stability either by ejecting a nuclear particle or by the emission of radiation.

As we have repeatedly stated, a neutron does not have to overcome a potential barrier in penetrating a nucleus. However, if a neutron-induced reaction causes the ejection of a charged particle, the latter will have to overcome a potential barrier to escape from the nucleus. Because of this barrier, charged particles are not usually emitted except with high-speed neutrons. The majority of elements when bombarded with neutrons are transmuted into unstable isotopes. These radioelements are always negative electron emitters except where the original nuclear reaction is an $(n,2n)$ type, in which case the isotope may sometimes be a positron emitter. Three general types of nonfission reactions have been produced with neutrons. They are:

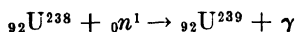
1. *Radiative Capture.* The (n,γ) is the most common nuclear reaction. It has been carried out for isotopes of practically all the elements. Many of the isotopes available from the Isotopes Division of the Atomic Energy Commission, which are important in many fields of research, are produced by this reaction. Two examples of neutron capture, in which the product is an electron emitter, are



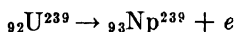
Among the most interesting of the radiative-capture reactions is the one involved in the production of the long-lived isotope of plutonium. In

372 Fundamental Concepts of Inorganic Chemistry

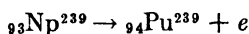
this reaction, thermal neutrons are captured by uranium-238 as follows:



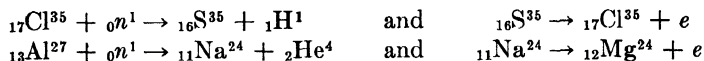
Uranium-239 has a short half life and decays with the emission of electrons (beta emission) to produce another radioelement, neptunium-239.



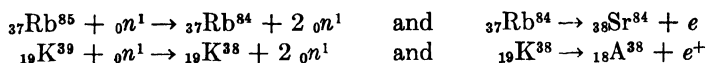
Neptunium-239 is also a beta emitter with a half life of 2.3 days, decaying into plutonium-239, which has a half life of 24,000 years.



2. Emission of Charged Particles. Because charged particles must penetrate a high potential barrier, such reactions are uncommon. However, reactions in which protons, deuterons, and alpha particles are ejected after neutron bombardment have been reported. As might be expected, reactions of this type are favored by neutrons with large kinetic energies. Examples are:



3. Emission of Neutrons. The binding energy of a nucleon is approximately 8 Mev; therefore reactions of the ($n,2n$) type would require the bombarding neutron to have a kinetic energy of at least 8 Mev or more. Radioelements produced in reactions of this type are either electron emitters or positron emitters. As was stated in Sec. 8-10, if the radioactive isotope has a smaller proton:neutron ratio in its nucleus than has the corresponding stable isotope, the particle emitted will be an electron. The emission of an electron will increase the proton:neutron ratio. On the other hand, if the proton:neutron ratio is higher than that in the stable isotope, the particle emitted will be a positron. The emission of a positron serves to decrease the proton:neutron ratio. Examples of nuclear reactions illustrating the formation of radioisotopes with the two types of behavior are

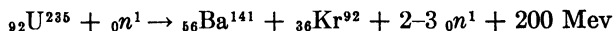


8-16 Nuclear Fission. Following the discovery of the neutron, Fermi and his coworkers used this particle as a projectile for bombarding the nuclei of most of the elements. Their investigations indicated that the majority of elements give unstable isotopes when bombarded with neutrons which have been slowed down by water or paraffin. Furthermore it was observed that neutron capture by a nucleus produced a radioisotope which invariably decayed by beta emission. Since beta decay

leads to an element with an atomic number greater than its parent, Fermi and his associates used uranium as a target element with the expectation that an element of atomic number 93 could be synthesized in the two-step process. In their first experiments at least four different beta activities, identified by their half lives, could be detected. These activities were attributed to the possible formation of a series of unstable elements with atomic numbers greater than 92, which were referred to as *transuranium elements*.

When the work of Fermi was repeated by other scientists, an even greater number of beta activities was obtained. Out of the confused interpretations of these experiments came the significant discovery by Hahn that one of the products produced by neutron bombardment of uranium was an isotope of barium. To Meitner goes the credit for correctly interpreting these results as a splitting of the uranium nucleus, after neutron capture, into two nuclear fragments. Later Meitner and Frisch predicted that nuclear fission of heavy elements should be accompanied by the release of large amounts of energy. This prediction was verified shortly afterward by a number of noteworthy experiments.

An examination of the binding-energy curve in Fig. 1-1 shows that heavy nuclei are more unstable (binding energy per nucleon is less) than those nuclei on or near the maximum of the curve. This curve indicates the possibility that heavy nuclei might be broken down into lighter and more stable nuclei. Up to 1947 fission had not been produced in any element of atomic number less than 90, but more recently fission has been accomplished by means of accelerated particles in elements with atomic numbers as low as that of tantalum. The most important fission reactions are those which are produced by neutron bombardment. However, the number of stable isotopes, in available quantities, which undergo fission with neutrons is not large. Thermal neutrons are effective in the fission of ${}_{92}\text{U}^{233}$, ${}_{92}\text{U}^{235}$, and ${}_{94}\text{Pu}^{239}$, whereas fast neutrons produce fission in ${}_{90}\text{Th}^{232}$, ${}_{91}\text{Pa}^{231}$, and ${}_{92}\text{U}^{238}$. A typical fission reaction involving uranium-235 may be illustrated by the equation



As indicated by the equation, the products are the nuclei of the lighter elements plus two to three excess neutrons and an enormous amount of energy. It should be emphasized that ${}_{56}\text{Ba}^{141}$ and ${}_{36}\text{Kr}^{92}$ are only 2 out of at least 160 isotopes of 40 or more different product elements which have been identified from this reaction. It has been observed that the products, resulting from fission induced by thermal neutrons, are always unequal in mass, with a ratio to each other of approximately 5:7. The range of mass numbers for the products are between 82 and 100 for the lighter nuclei and between 128 and 150 for the heavier ones. The fission-

yield curve given in Fig. 8-3 shows that the maxima for the products occur at points where the mass numbers are 95 and 139. The minimum fission yield appears at 117, and since this is a logarithmic curve, the minimum is approximately one six-hundredth the values of the maxima.

Because the neutron:proton ratio for the heavy nuclei which undergo fission is greater than the ratio for the nuclei of the products, it is to be expected that a fission reaction will yield excess neutrons. The average number of neutrons per fission has been stated as about 2.3, and these account for about 2 per cent of the total fission energy. Despite the neutrons produced in the reaction, the fission fragments usually have neutron:proton ratios higher than those for stable isotopes. Consequently, as described in Sec. 8-15, these nuclei strive toward stability by emitting electrons. Sometimes as many as six successive beta decays are necessary for the fission products to achieve stability.

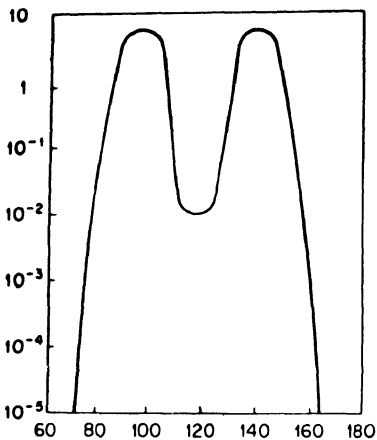


Fig. 8-3 Fission-yield curve for uranium-235 with slow neutrons.

The great interest in nuclear fission results from the tremendous energy associated with the process. Until 1939 the largest release of energy in a nuclear process was of the type described in Sec. 8-11, where two light

atoms combine to produce two helium atoms, with a loss of mass for the total process. In the fission of uranium-235 a much greater mass is converted into energy. The amount of mass so converted has been calculated to be about 0.215 mass unit per uranium nucleus. Since 1 mass unit is equivalent to 931 Mev, then $0.215 \times 931 = 198$ Mev for each uranium nucleus. Approximately 80 per cent of this energy appears as kinetic energy of the fission fragments, and most of the remainder is released in subsequent radioactive processes. It is beyond the scope of this book to discuss the production and utilization of nuclear energy, but it should be pointed out that the only naturally occurring nuclear fuel is uranium-235. This key material may be used with fertile materials (isotopes which can be converted into fuels, such as uranium-238 and thorium-232) to produce other nuclear fuels, as, for example, plutonium-239 and uranium-233.

As long ago as 1930, Gamow used the analogy of a drop of liquid to explain the behavior of a nucleus. Since that time it has been convenient to use this analogy in describing the process of nuclear fission. The

strong nuclear forces which hold nucleons together may be postulated as causing a nucleus to assume a spherical shape in a manner similar to the cohesive forces within a liquid drop. In a heavy nucleus the large number of protons may add up to sizable forces of repulsion which strive to elongate the drop. It will be recalled from Sec. 1·12 that nuclear forces operate only over short distances, and in a heavy nucleus these forces are weakened by its size. There appears to be a balance between the repulsive forces of a large number of protons and the attractive forces produced by nuclear binding, the latter being weakened on account of the mass of the nucleus. Bohr and Wheeler have shown, mathematically,

TABLE 8-8 EASE OF FISSION AS RELATED TO NUCLEON COMBINATIONS

Constitution of nucleus		Relatively stable isotopes	Fissioned by
Neutrons	Protons		
Even	Even	${}_{90}\text{Th}^{232}$, ${}_{92}\text{U}^{238}$	Fast neutrons
Even	Odd	${}_{91}\text{Pa}^{231}$, ${}_{93}\text{Np}^{237}$	Fast neutrons
Odd	Even	${}_{92}\text{U}^{233}$, ${}_{92}\text{U}^{235}$, ${}_{94}\text{Pu}^{239}$	Slow neutrons
Odd	Odd	Unstable	No record

that there should be a critical size for nuclei, above which the forces of repulsion will be greater than the forces holding the nucleus together. In terms of a slightly elongated drop the two ends have positive charges tending to force the drop into a dumbbell shape and thereby producing fission. The two charged portions of the drop are designated as Z each, and this value is directly related to the atomic number. The ease of fission apparently has some connection with the ratio of Z^2/A , where A is the mass number. In their computations, Bohr and Wheeler arrived at a figure of 45 as a critical value for Z^2/A . At this point, according to their calculations, the forces of electrostatic repulsion are sufficiently large to cause fission to take place. A value of 45 for Z^2/A indicates an atomic number of 120 as the upper limit of nuclear stability. In view of the fact that the stabilities of the transuranic elements of atomic numbers in the neighborhood of 100 are quite low, an upper limit of 120 would appear too high. Actually there is some doubt as to the possibility of synthesizing the remaining element of the actinide series. The completion of this series would demand an element with an atomic number of 103.

Long before the fission of heavy nuclei it was recognized that the stabilities of isotopes were dependent upon certain neutron-proton combinations. For example, the most stable isotopes occurring widely in nature are those whose nuclei contain an even number of neutrons and an even number of protons. The number and occurrence of isotopes in nature as

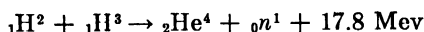
376 Fundamental Concepts of Inorganic Chemistry

related to the constitution of their nuclei are given in Table 1·7. The rules given in Sec. 1·18, which appear to predict the stabilities of naturally occurring isotopes, apparently hold true also for isotopes of heavy nuclei. For example, nuclei with an even-even number of neutrons and protons require fast-moving neutrons for fission, whereas an odd-even combination of neutrons and protons may be fissioned with slow neutrons. An odd-odd combination should be even more easily fissioned, but isotopes of this combination are so unstable that the possibility of their fission has not been explored. Table 8·8 presents these facts in a tabular form.

8·17 Nuclear Fusion. The fission of heavy nuclei into smaller fragments releases an enormous amount of energy. This energy has been calculated to be approximately 200 Mev/atom for uranium-235. If one atom of uranium is fissioned by one neutron, the per cent efficiency in terms of mass converted into energy (where 1 mass unit = 931 Mev) is

$$\frac{200 \text{ Mev}}{(235 + 1) \text{ mass units} \times 931} \times 100 = 0.09\%$$

Energy is also released when nuclei of light elements fuse to produce less energetic nuclei. It has been stated that the so-called "hydrogen bomb" may gain its detonation energy from a reaction between deuterium and tritium. The equation for the reaction is

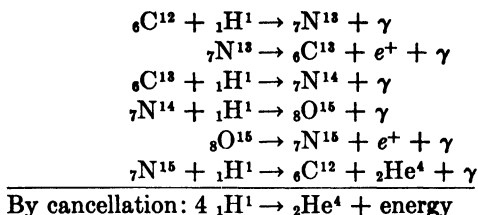


In terms of whole numbers this reaction involves the fusion of 5 mass units to release 17.8 Mev of energy. The efficiency of the energy conversion is approximately

$$\frac{17.8 \text{ Mev}}{5 \text{ mass units} \times 931} \times 100 = 0.35\%$$

The foregoing calculations indicate that for these two fission and fusion reactions the per cent efficiency is approximately four times greater for the fusion reaction. Other comparable reactions give efficiency comparisons within the same range. Considerable interest has been focused upon fusion reactions as a source of atomic energy. It is regrettable that men's first interest in this direction has been for the purpose of creating a thermonuclear weapon, but there is considerable evidence that fusion reactions will eventually be harnessed for industrial power.

The energy source of the stars, including our sun, is believed to be derived from a complex chain of nuclear transformations, which, when simplified by cancellations, amounts to the union of four hydrogen atoms to form one helium atom. This series of reactions, as proposed independently by Weizäcker and Bethe in 1938, may be indicated by equations as follows:



The end result, in the cycle of reactions, is the conversion of four hydrogen nuclei into one helium nucleus, and the final reaction is exoergic to the extent of 26.8 Mev/cycle. On the other hand a temperature of approximately 20,000,000°C is necessary for the reactions to take place, and it has been estimated that 6 million years are required for the completion of a single cycle. Obviously the temperature and time cycle for the conversion of hydrogen into helium by the foregoing reactions would indicate that such reactions are totally unsuited for man-made experimentation. Not until the atomic bomb had been developed was interest redirected to stellar nuclear reactions as a possible source of energy.

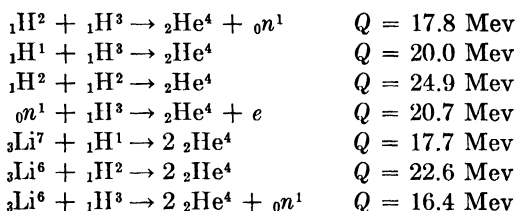
The mean thermal kinetic energy of an alpha particle at room temperature is of the order of 10^{-2} ev, but at the temperature of 10,000,000°C (the temperature of our sun) the kinetic energy is increased to about 10^4 ev. The multiplication of kinetic energy by 1 million times is equivalent to the acceleration which may be accomplished in a cyclotron or similar devices. The nuclei of light atoms exert strong electrostatic repulsion toward each other. Yet at a temperature of 1,000,000°C the kinetic energies of light atoms are sufficiently large so that they are enabled to overcome their own potential barriers and enter into nuclear reactions with each other. The temperatures which may be obtained by the fission of either uranium or plutonium in the critical quantities utilized in atomic bombs is at least 1,000,000°C. Consequently a fission reaction is used as a thermonuclear "match" to ignite certain fusion reactions. However, the cycle of reactions which has been postulated as taking place in the sun requires a higher temperature than may be obtained from the fission of heavy nuclei. Also, the 6 million years required for the cycle makes it totally impractical as an energy source on earth. There are, however, other fusion reactions which take place at lower temperatures and with greater speeds. The ideal reaction is one which takes place very rapidly and at a comparatively low temperature. Furthermore it should release a large amount of energy. A comparison of a few fusion reactions as to the energy released and the rate of the reaction are given in Table 8-9.

Of all the possible reactions that may take place among hydrogen isotopes, the most energetic are those in which the helium nucleus, ${}^2_2\text{He}^4$, is

TABLE 8-9 NUCLEAR REACTIONS INVOLVING THE FUSION OF ISOTOPES OF HYDROGEN

Nuclear reaction	Energy released, Mev	Time
${}_1\text{H}^1 + {}_1\text{H}^1 \rightarrow {}_2\text{H}^2 + e^+$	1.4	10^{11} years
${}_1\text{H}^2 + {}_1\text{H}^1 \rightarrow {}_2\text{He}^3 + \gamma$	5	0.5 sec
${}_1\text{H}^3 + {}_1\text{H}^1 \rightarrow {}_2\text{He}^4 + \gamma$	20	0.05 sec
${}_1\text{H}^2 + {}_1\text{H}^2 \rightarrow {}_2\text{He}^3 + {}_0n^1$	3.2	3×10^{-5} sec
${}_1\text{H}^2 + {}_1\text{H}^2 \rightarrow {}_1\text{H}^3 + {}_1\text{H}^1$	4	3×10^{-5} sec
${}_1\text{H}^3 + {}_1\text{H}^2 \rightarrow {}_2\text{He}^4 + {}_0n^1$	17.8	1.2×10^{-6} sec

the end product. This is to be expected because the mass of the helium nucleus is small, indicating that mass has been converted into energy in its formation from hydrogen isotopes. The actual reaction which is utilized in the hydrogen bomb is not public information; however, a number of possibilities are offered in the following equations:



THE TRANSURANIC ELEMENTS

Elements with atomic numbers higher than uranium do not occur in nature except in minute traces, as in neptunium and plutonium, resulting from the action of stray neutrons upon uranium ores. However, six elements with atomic numbers 93 to 98 have been synthesized and their properties fairly well explored during and since World War II. The more recently discovered elements 99, 100, 101, and 102 are still under investigation.

During the period 1934–1935 Enrico Fermi and his coworkers discovered that the majority of elements when treated with slow neutrons were converted into radioactive products which emitted electrons upon decay. The emission of an electron, in beta decay, leads to the transmutation of the element into a different element with an atomic number one unit higher. Fermi and his associates used uranium as a target element, expecting that the end product would be a new element with an atomic number of 93. Their actual product, or products, was not one but several beta emitters, which they attempted to explain as the formation of a series of “transuranic” elements with atomic numbers higher

than that of uranium. Later investigations proved that this interpretation of their results was erroneous (Sec. 8-16); however, these experiments do represent the first recorded attempt to synthesize elements with atomic numbers above uranium.

The transuranic elements differ from other elements in that they are all synthetic; yet they constitute a part of the actinide series of the rare earths. An examination of a periodic classification of the elements reveals the presence of two groups of elements which do not fit into the main body of the classification. These two groups are composed of elements whose atoms contain three incomplete electronic shells. The elements within each group are very similar in their chemical properties because the differentiating electrons of their atoms are in the third from the outermost shell. The two series are designated as the *lanthanide* and *actinide* series after the first element in each group. Previous to 1940 only three elements of the actinide group were known; therefore, it is not surprising that the existence of a second group of rare earths was not suspected until other members of the series were discovered. In 1945 G. T. Seaborg of the University of California at Berkeley suggested that those elements with atomic numbers of 89 and beyond should constitute a second group of inner transition elements. However, the elements within this group show a much wider variation in oxidation states, and thereby greater differences in chemical properties, than do those belonging to the lanthanum series.

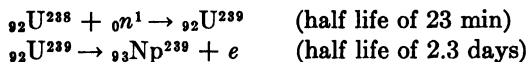
Despite the fact that ten transuranium elements have been discovered and the first six have been investigated rather extensively as to their chemical properties, only one of these elements—plutonium—has been prepared in quantity. The others have been studied first as tracers and later by ultramicrochemical techniques. The latter approach has been pioneered by A. A. Benedetti-Pichler and P. L. Kirk. An excellent description of these methods is found in a volume prepared by Dr. Kirk.¹ The dangerous level of alpha activities for isotopes of the transuranic elements, with the exception of neptunium-237, renders these radioelements unsafe to handle without special equipment. For this reason it is highly unlikely that compounds of these elements, except the stable isotope of neptunium, will ever be used as ordinary laboratory reagents.

8-18 Neptunium. The first transuranium element was discovered by E. M. McMillan and P. H. Abelson at the University of California in 1940. Upon bombarding a layer of uranium oxide with slow neutrons obtained from the cyclotron of E. O. Lawrence, they were able to prepare a radioisotope of neptunium with a half life of 2.3 days. This isotope was recognized as a beta-decay product of a radioisotope of uranium with

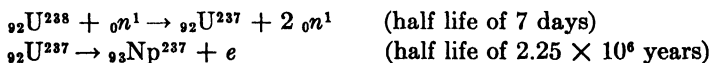
¹ P. L. Kirk, "Quantitative Ultramicroanalysis," John Wiley & Sons, Inc., New York, 1949.

380 Fundamental Concepts of Inorganic Chemistry

a half life of 23 min. The nuclear equations for these reactions may be indicated as



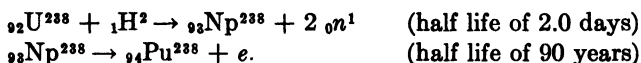
A more stable isotope of neptunium, Np^{237} , was discovered by G. T. Seaborg and A. C. Wahl in 1942, which was later prepared in weighable amounts. The product is formed by the action of high-speed neutrons in an $(n,2n)$ -type reaction and is an alpha emitter with a half life of 2.25×10^6 years. It is recognized as the progenitor of the neptunium $(4n + 1)$ series of radioactive elements (Sec. 8·7). This comparatively stable isotope is prepared according to the nuclear equations



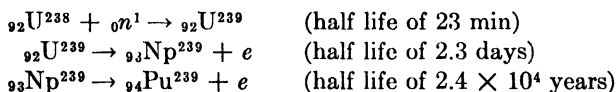
The long half life of the isotope has evoked the suggestion that the atomic weight of neptunium should be considered as that of mass number 237.

The chemical properties of neptunium are similar to those of uranium. Both have oxidation states of III, IV, V, and VI, but neptunium differs from uranium in that it is more difficult to oxidize to the higher oxidation states. Consequently the most stable compounds of neptunium are those of the IV oxidation state, whereas those of uranium are the VI oxidation state. Neptunium ions in aqueous solution display characteristic colors: pale purple for Np^{3+} , pale yellow-green for Np^{4+} , green-blue for Np^{5+} , and pink or yellow-green for NpO_2^{++} depending upon the acidity of the solution. Important halides of neptunium are NpF_3 , NpF_4 , NpF_6 , NpCl_3 , NpCl_4 , NpBr_3 , NpBr_4 , and NpI_3 . The precipitation reactions of Np^{3+} and Np^{4+} are similar to the corresponding trivalent and tetravalent rare earths of the lanthanide series, as, for example, the cerous and ceric ions.

8·19 Plutonium. The second transuranium element to be discovered was element 94, later named *plutonium* after the planet Pluto in accordance with the convention used in naming uranium and neptunium. This element was synthesized and identified by G. T. Seaborg, E. M. McMillan, A. C. Wahl, and J. W. Kennedy in 1940. The first isotope to be produced was the one with mass number 238, formed by the deuteron bombardment of uranium-238. The first product of this bombardment is the 2.0-day beta-emitting radioisotope of neptunium, Np^{238} , which decays to plutonium-238 with a half life of about 90 years. The two-step reaction involves a $(d,2n)$ transmutation followed by a beta decay which may be indicated as



The most important isotope of plutonium is the one that was sought by McMillan and Abelson as a decay product of neptunium-239 (Sec. 8-18). Using large amounts of the short-lived beta-decaying neptunium isotope, J. W. Kennedy, G. T. Seaborg, E. Segrè, and A. C. Wahl identified the decay product as plutonium-239. Because of the great importance of this isotope and its synthesis, the complete equations for its preparation are repeated as follows:



Plutonium-239 is fissionable with slow neutrons, which places it in the same class with uranium-235 as a nuclear fuel. The fact that it can be produced more cheaply than uranium-235 should result in its becoming an important source of atomic energy. This isotope was the explosive constituent of the atomic bomb which was dropped on Nagasaki in 1945.

Sizable quantities of plutonium have been prepared and stockpiled in anticipation of usage in thermonuclear weapons and as a fuel for nuclear reactors in the production of industrial power. Inasmuch as the preparation involves a considerable knowledge of plutonium chemistry, the properties and reactions of this element have been thoroughly investigated.

Despite the fact that plutonium-239 is a long-lived isotope with a half life of 24,000 years, its alpha activity is still sufficiently dangerous so that neither the element nor its compounds can be handled on a macroscale without special equipment and extreme care. The radioactivity amounts to approximately 140 million alpha disintegrations per minute per milligram of material, which can be destructive to living tissues. Because of this hazard most experimental investigations with plutonium have been on a microscale even though larger quantities have been available.

According to Seaborg's hypothesis, which has been substantiated by considerable experimental evidence, the transuranium elements are part of a second rare earth group beginning with actinium, in which the 5f electron orbitals are being filled in subsequent elements. It is to be expected, therefore, that the members of this group should be closely related chemically. However, the newly developed actinide series differs from the more familiar rare earth series, beginning with lanthanum, in that the resemblance of successive elements is somewhat less pronounced. For example, the lanthanide earths are, for the most part, amenable to separation only by multiple fractionation processes or by absorption and elution through ion-exchange resins. On the other hand, the elements 89 to 95 may be separated by oxidation-reduction processes, although the elements beyond 95 appear to require the same complex methods of

separations that characterize the lanthanide group. The chemistry of plutonium resembles that of uranium except that the stable oxidation state of plutonium is IV, whereas that of uranium is VI. It is this difference which permits a chemical separation of plutonium and uranium. The +4 oxidation state is even more stable for plutonium than for neptunium as evidenced by the fact that the latter is susceptible to bromate oxidation to the VI oxidation state, while plutonium is not. However, these separations are far from simple. In removing plutonium from the various materials with which it is mixed as it comes from a reactor pile at least 30 major chemical reactions involving hundreds of operations are necessary.

Plutonium ions show characteristic colors in aqueous solutions: blue-lavender for Pu^{3+} , yellow-brown for Pu^{4+} , and pink-orange for PuO_2^{++} . The trivalent plutonium ion can be precipitated as the hydroxide and fluoride, and the same ion is readily oxidized in air to the tetrapositive state. In this latter state are found most of the stable compounds of plutonium. Among these relatively stable quadrivalent compounds are the fluoride, the iodate, and the hydroxide, which are all insoluble in water, as well as the soluble compounds of the chloride, nitrate, perchlorate, and sulfate. Excess of various anions, such as the oxalate, phosphate, sulfate, and fluoride, may act as chelating agents toward trivalent and quadrivalent plutonium ions, and even the nitrate and chloride ions may have some chelating affect on the quadrivalent and hexavalent ions. In addition, certain organic reagents, as for example diketones, may act as chelating agents to form complexes that are soluble in organic liquids.

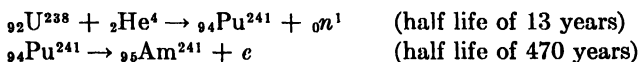
The most stable oxide of plutonium is the dioxide. Practically all plutonium compounds are converted into PuO_2 when ignited in air to temperatures above 1000°C . The inertness of the greenish-yellow dioxide makes it a satisfactory compound for the gravimetric determination of plutonium. The dioxide may also serve as a starting material for the synthesis of other compounds of plutonium.

The foregoing description of the chemical properties of plutonium is far from complete. In view of the probable future importance of this element an increasing emphasis upon its chemical properties may soon be in order. Much information about plutonium and other transuranium elements is contained in the two-volume set of research papers edited by Seaborg, Katz, and Manning.¹

8-20 Americium. The third transuranium element was the fourth to be discovered. It was identified by G. T. Seaborg, R. A. James, and L. O. Morgan in 1944. Seaborg in naming americium said: "We suggest for the element 95, with its six 5f electrons, the name *americium*, or New

¹ G. T. Seaborg, J. J. Katz, and W. M. Manning, "The Transuranium Elements," McGraw-Hill Book Company, Inc., New York, 1950.

World, by analogy with europium, with its six 4f electrons, which was named for Europe." The new element was synthesized by bombarding uranium-238 with high-speed (40 Mev) alpha particles from a cyclotron and first producing a fairly long-lived beta-emitting isotope of plutonium, Pu^{241} , which decays to form the alpha-emitting isotope of americium, Am^{241} , with a half life of approximately 500 years. The equations for these nuclear reactions are



The isotope Am^{241} emits alpha particles and has a half life of nearly 500 years. The alpha activity of this species is approximately 70 billion alpha emissions per minute per milligram, which makes it necessary to carry out all experimental investigations with certain precautions and special techniques. A less dangerous and more stable isotope has since been discovered with a half life of approximately 10,000 years. The more stable isotope, Am^{243} , may be expected to play a prominent role in the elucidation of americium chemistry.

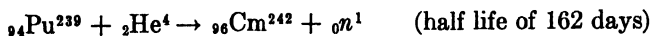
Early work employing tracer technique led to the conclusion that americium existed in aqueous solution only in the trivalent state. Later work with milligram quantities indicates that this element may exist in acidic aqueous solution in the III, V, and VI oxidation states, with some evidence that the ions corresponding to these states are Am^{3+} , AmO_2^+ , and AmO_2^{++} . However, from the oxidation potentials which have been determined for these states, it may be said that the trivalent state is quite stable in aqueous solution and extremely difficult to oxidize or reduce. This ion is more easily oxidized in alkaline solution.

Trivalent americium behaves in its precipitation reactions in an analogous fashion to the trivalent actinide and lanthanide elements. Accordingly the fluoride and oxalate are insoluble, whereas the iodate and phosphate are only fairly soluble in water. On the other hand, the nitrates, sulfates, sulfides, and halides are all soluble. The existence of the +6 state was verified by the crystallization of the compound $\text{NaAmO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$, which is isostructural with the +6 compounds of uranium, neptunium, and plutonium. Trivalent americium may be precipitated as the insoluble hydroxide from aqueous solutions, and when this compound is ignited in air, a black oxide with the formula AmO_2 is produced. The latter compound may be reduced by hydrogen to an orange-red oxide with a composition of Am_2O_3 . An effective separation of americium from rare earth elements has been developed through ion-exchange-resin methods.

8-21 Curium. The fourth transuranic element, atomic number 96, was the third to be discovered. It was identified by G. T. Seaborg,

384 Fundamental Concepts of Inorganic Chemistry

R. A. James, and A. Ghiorso in 1944 as a product obtained by bombarding plutonium-239 with alpha particles from the Berkeley cyclotron. The new element was named according to the convention by which the analogous lanthanide element, gadolinium, was named. Gadolin was the Finnish chemist famed for his early work in the rare earth field. The new element was named *curium* in honor of Marie and Pierre Curie, who were pioneers in the field of natural radioactivity. The reaction by which the first isotope, Cm^{242} , was prepared may be indicated as

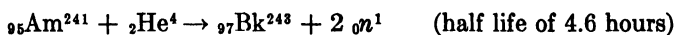


The very short half life of this alpha-emitting isotope makes it extremely hazardous for investigation. The specific alpha activity is approximately 10^{14} disintegrations per minute per milligram. Not only is this activity dangerous to living tissues, but it also represents a problem because of the effect of alpha emission upon carrier liquids. Other longer-lived isotopes have been reported. One of these is Cm^{243} , with an estimated half life of 100 years, which should offer a safer vehicle for the exploration of curium chemistry.

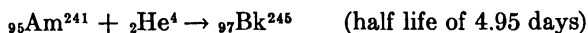
The trivalent oxidation state of curium is extremely stable, and there is no experimental evidence that higher or lower oxidation states may exist. Because of this inertness toward oxidizing and reducing agents it may be separated from other transuranic elements by a combination of oxidation and precipitation methods. The trivalent curium ion behaves like a typical rare earth element of this oxidation state. The fluoride and oxalate are insoluble in acid solution, whereas the nitrate, sulfate, sulfide, and halides are all soluble. Curium does not impart a color to its solutions, although it does absorb color in the ultraviolet region. In this respect it is quite similar to its homologue, gadolinium, in the lanthanide series.

8-22 Berkelium. Berkelium, the eighth member of the actinide transition series and the fifth transuranic element, was discovered in late 1949 by S. G. Thompson, A. Ghiorso, and G. T. Seaborg. It was named in honor of Berkeley, Calif., where the discovery of this and other transuranic elements was made. The selection of the name follows the same pattern used in naming curium and americium. The rare earth homologue of berkelium in the lanthanide series is terbium, which was named for Ytterby, Sweden, where a number of rare earth minerals have been found. The new element, with atomic number 97, was synthesized by bombarding americium-241 with high-speed alpha particles from the Berkeley cyclotron. The first isotope to be identified was Bk^{243} , with a half life of 4.6 hr, which apparently decays by orbital-electron capture. The nuclear reaction for the synthesis of the element number 97 may be

indicated as



Another isotope, Bk^{244} , is produced with less energetic alpha particles, and this species has about the same half life as the first isotope, just described. A longer-lived isotope, Bk^{245} , has been synthesized by Seaborg and his coworkers in a similar reaction in which alpha particles are captured without neutron emission. The result is



The chemical properties of berkelium have been studied only in tracer quantities. This technique is usually indicative, but it is certainly never more than qualitative. It appears that berkelium may exist in aqueous solution in the tripositive and tetrapositive states. The solubilities of its compounds are quite similar to those of the other inner transition elements in the same oxidation states. It is characteristic of these elements that the fluoride and oxalate should be insoluble in acid solution, the iodate and phosphate fairly insoluble, and the nitrate, sulfate, sulfide, and halides always soluble.

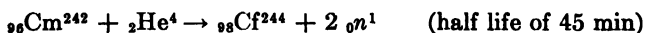
The behavior of trivalent berkelium on elution (extraction) following its adsorption by an ion-exchange resin is considered to be significant by Seaborg and his coworkers. They have secured evidence that there is a break between berkelium and curium in the elution curve analogous to a similar break between terbium and gadolinium. To them this comparable behavior indicates that the two series have analogous breaks in ionic radius, or, in other words, a change in ionic size occurs at the same mid-point in the two rare earth series. The change in rate of elution (and consequent change in ionic radius) constitutes additional evidence for the existence of the second group of inner transition elements.

8.23 Californium. The ninth member of the actinide series, which is also the sixth transuranic element, was discovered in 1950 by S. G. Thompson, K. Street, Jr., A. Ghiorso, and G. T. Seaborg. The element was named *californium* in honor of the university and state where the work was done. There is no analogy between the naming of this element and that of its rare earth homologue, dysprosium. The latter was named after the Greek term meaning *difficult to get at*, and the name *californium* seems meaningless in relation to such a description.¹ The new element was produced by bombarding microgram amounts of curium-242 with 35-mev alpha particles from the Berkeley cyclotron. The first isotope to be identified was Cf^{244} , which has a half life of 45 min. The synthesis of

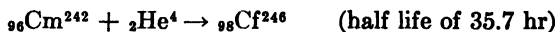
¹ Seaborg has made the wry comment that California was "hard to get at" for the early pioneers.

386 Fundamental Concepts of Inorganic Chemistry

this isotope of element number 98 may be indicated as

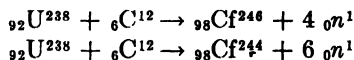


Less energetic alpha particles produce a longer-lived isotope, Cf^{246} , with a half life of 35.7 hr.



The chemical properties of californium have been investigated only through work with tracer amounts. The qualitative results so obtained indicate that the trivalent ion is very stable in aqueous solution. This oxidation state has resisted efforts to reduce or oxidize it, but when these experiments are repeated with larger amounts of materials, it is possible that other oxidation states may be obtained. The solubilities of the compounds formed by the trivalent ion appear to be analogous to those of other inner transition elements in the corresponding oxidation state. These have been listed for several of the transuranic elements in preceding sections.

Isotopes of the transuranium elements have been prepared by utilizing a technique whereby ions such as carbon and nitrogen nuclei are accelerated in the cyclotron and concentrated as high-energy beams on target materials. In this manner the atomic number and mass of the element under bombardment may be increased by several units in one step. The preparation of the two isotopes of californium by bombarding uranium-238 with high-speed carbon nuclei illustrates this technique. The equations for these nuclear processes are

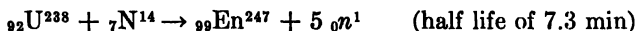


8-24 Other Transuranic Elements. Elements with atomic numbers 99, 100, 101, and 102 have been discovered. The investigations involving elements 99, 100, and 101 were carried out at the University of California, the Argonne National Laboratory, and the Los Alamos Scientific Laboratory. Element 102 was produced as the result of a joint effort by the Argonne laboratory, Britain's Harwell laboratory and Sweden's Nobel Institute for Physics. Some of the work is still classified,¹ and until more information becomes available, it is impossible to give a complete picture of these discoveries. At present, credit for the discovery of element 101 has been given to Albert Ghiorso, G. B. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg. It is quite likely that Seaborg and his coworkers will also receive credit for either discovering or jointly discovering elements 99 and 100. Scientists taking part in the synthesis of element 102 included Paul R. Fields, group leader in Argonne's chemistry

¹ Information which is held confidential for security reasons.

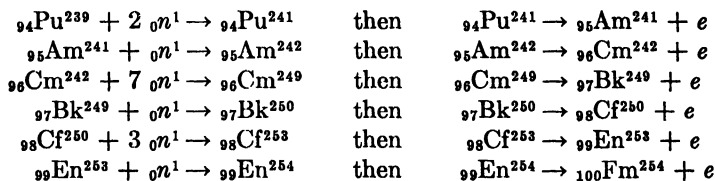
division; John Milsted of Harwell, and the Nobel team of Huga Atterl ng, Bjorn Astron, Wilhelm Forsling, and Lennart Holm.

Einsteinium has been proposed for the name of element 99 in honor of Albert Einstein, world-famous mathematician and physicist. This element has been prepared by bombarding uranium-238 with nitrogen nuclei accelerated in the Berkeley cyclotron. The isotope prepared in this manner is En^{247} , which is an alpha-emitting particle with a half life of 7.3 min. The one-step synthesis may be indicated as



Using tracer techniques involving lanthanum fluoride as a carrier, ion-exchange resins for separation, and radioactive pattern for identification, it has been possible to separate and characterize this element as a member of the actinide series with an atomic number of 99. It is similar to holmium of the lanthanide series in its chemical properties.

Fermium is the name suggested for element 100, in honor of Enrico Fermi, the brilliant Italian physicist (later at the University of Chicago), who pioneered the syntheses of elements by neutron bombardment. He also played an important role in the development of the theory of nuclear fission. Discovery of element 100 was announced simultaneously by a research team of scientists at the Argonne National Laboratory and the Seaborg team at the University of California. The first production of an isotope of element 100 took place in an atomic reactor. This is the first element with an atomic weight above that of curium to be prepared in such a manner. Other elements were produced by cyclotron bombardment. The synthesis involved the transmutation of plutonium by means of neutron irradiation to the isotope ${}_{100}\text{Fm}^{254}$. In this complicated procedure 15 neutrons are absorbed by each atom of the original plutonium, and during the process 6 beta particles (electrons) are emitted. It should be added that one of the intermediate products within the synthesis is an isotope of einsteinium (element number 99) with a mass number of 253. The reaction chains leading to elements 99 and 100 are



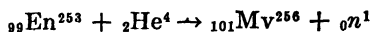
A Swedish group of scientists at the Nobel Institute of Physics in Stockholm has succeeded in making an isotope of element 100 by bombarding uranium-238 with 180-Mev oxygen particles in a cyclotron. The isotope has an estimated half life of about 30 min. The nuclear reaction

could be indicated by the following equation, although it is probably not so simple:



As may be expected, many of the properties of fermium are similar to those of erbium, the corresponding homologue, in the first group of inner transition elements.

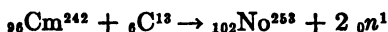
Mendelevium has been adopted as the name of element 101 in honor of Dimitri Mendeleev, the first to use the periodic system of the elements to predict the chemical properties of undiscovered elements. This element was discovered by A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg. The synthesis was accomplished by bombarding fermium-253 with 41-Mev alpha particles. Inasmuch as ${}_{99}\text{En}^{253}$ has a half life of only 20 days, it was necessary that the experiment should not be prolonged. Actually the target element was electroplated on the back of thin gold foil so that alpha particles passing through the foil might be captured by the atoms in the einsteinium layer. The magnetic field of the cyclotron was altered in a manner so that it was possible to deliver an extraordinarily intense beam of alpha particles upon a small target area. It was estimated that an area of $\frac{1}{32}$ by $\frac{1}{4}$ in. of target was subjected to 30 trillion alpha particles per second. After bombardment the collecting foil was dissolved, the gold and impurities removed, and the remaining material separated into fractions consisting of element 99, element 100, and element 101. The first isotope to be prepared, ${}_{101}\text{Mv}^{256}$, has a half life between a half hour and several hours. It is unusual in that it appears to decay by spontaneous fission. The equation for the preparation may be indicated as



The chemical properties of mendelevium appear to be similar to those of the rare earth thulium, which is the corresponding element in the first inner transition series.

Nobelium has been suggested as the name of element 102 inasmuch as the element was first synthesized at the Nobel Institute of Physics in Stockholm, Sweden. The production of the new element resulted from the cooperative efforts of members of an international research team from three countries. Scientists from the United States Atomic Energy Commission's Argonne National Laboratory contributed the element curium, itself synthetic, which was used as the target in the atomic synthesis; English scientists from Harwell furnished the element carbon-13, a rare isotope from which positively charged carbon nuclei were obtained for use as atomic missiles; and Swedish scientists at Stockholm provided the cyclotron which had been especially constructed for this type of atomic bombardment.

Successful experiments in the synthesis of element 102 were carried out in Stockholm during March, 1957, and the official announcement of this discovery was made in June of the same year. The element was synthesized by bombarding a target containing curium, which was actually a thin layer of curium sandwiched between two layers of aluminum foil, with 110 to 120 Mev ions of carbon-13. The isotope of element 102 so produced was found to be an alpha emitter with a half life of 10 to 12 minutes. Its mass number is believed to be 253, although it is possible that it may be 251. The equation for the nuclear reaction may be



This isotope of the element 102 disintegrated so rapidly that the major problem was to prove that it had been created. Since only about 50 atoms of the new element were produced, it was necessary to develop special techniques to measure the alpha emission of these atoms before they disappeared completely. It has been said that the discovery of element 102 involved as much footwork and manual dexterity as it did physics.

Experimental evidence shows that isotopes with mass numbers 256 of both elements 100 and 101 decay by spontaneous fission. It has been predicted that all even-mass nuclei of even-atomic-numbered elements, such as 102 and 104 will decay even more rapidly by spontaneous fission. Apparently new elements, which may be discovered in the future, will probably have odd-mass nuclei. For some time there has been speculation that element 102 might be synthesized by bombarding a target of plutonium-239 with oxygen ions. The actual discovery of this element by bombarding curium-242 with carbon-13 ions follows the principle of such speculation. It is also possible that element 103 might be synthesized by bombarding a target of americium-241 with oxygen ions in a manner similar to the one used by the Swedish scientists in preparing element 100. However, the limit of nuclear stability in terms of atomic number and atomic mass is near at hand. As has been said before, one of the major problems in synthesizing element 102 was the identification of the few atoms that were prepared before they disappeared. Even greater feats of footwork and manual speed will be necessary in identifying elements with higher atomic numbers. For this reason it is safe to predict that very few additional elements will be synthesized and identified. An incidental note of interest is the fact that element 103, if prepared, should complete the second group of inner transition elements.

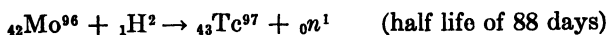
DISCOVERY OF CONTROVERSIAL ELEMENTS

At the present time there is no evidence that elements with atomic numbers 43, 61, 85, and 87 exist in nature except as minute traces in the

form, of short-lived intermediates in one or more of the nuclear decay chains. Yet there have been many claims to the discovery of these elements in nature, and names have even been assigned to them. Many of the publications which have appeared concerning these elements, especially element 61, reveal the fact that scientists have not always been torchbearers in their search for knowledge. Some of the claims, counter-claims, and often attacks might well have been left unpublished.

8-25 Technetium. In 1925 Noddack, Tacke, and Berg announced the discovery of element 43, to which they gave the name *masurium* after an ancient name for Prussia. Their claim for the discovery was based upon the X-ray emission spectra which they obtained from concentrates of platinum ores, columbite, sperrylite, gadolinite, fergusonite, tantalite, and various other minerals. Element 75, to which they gave the name *rhenium*, was discovered at the same time, and their work in connection with this element was verified by subsequent investigations. In fact this metal and its compounds are now available on a commercial basis. In the case of masurium the story has been quite different. Since the first claim for its discovery, no one has been successful either in duplicating the original work or in establishing the existence of element 43 in nature by any other means. However, as a result of the rapid development of rhenium chemistry, the discovery of masurium was not questioned for a number of years. Also, because of a lack of numerous claims and counter-claims, element 43 was never a truly controversial element.

Element 43 was discovered in 1937 by C. Perrier and E. Segrè and was given the name *technetium*, meaning *artificial*, in recognition of the fact that it was the first element to be made artificially. Working in Italy, the two investigators isolated and studied a radioactive isotope of element 43 which they extracted from an old molybdenum deflector plate that had been used in the 37-in. cyclotron at Berkeley, Calif. The molybdenum specimen had been subjected to bombardment with deuterons, as well as neutrons which were produced incidentally. The first isotope of technetium to be isolated and identified by Perrier and Segrè was Tc^{97} , with a half life of 88 days, which may be produced by bombarding molybdenum-96 with high-speed deuterons. The reaction is



A more stable and useful isotope, Tc^{99} , was discovered in the United States by G. T. Seaborg and E. Segrè in 1939. This isotope was produced by the interaction of Mo^{98} with slow neutrons (Mo^{99} is an intermediate product) and has a half life of 5×10^5 years. The equation for the nuclear reaction is



Wu and Segrè later found the same isotope of technetium among the fission products of uranium, from which an approximate yield of 6 per cent was indicated. Macroconcentrations of Tc^{99} show the element to have chemical properties intermediate between those of manganese and rhenium. The stability of the +7 oxidation state is greater than that of manganese and less than that of rhenium. The sulfide, Tc_2S_7 , which is dark brown in color, precipitates from 4 *M* H_2SO_4 and is quite insoluble. The pertechnetate ion, TcO_4^- , resembles the permanganate ion in that it imparts a pink color to its solutions.

8-26 Promethium. The discovery of element 61 was a subject of controversy for over two decades. Even the final naming was a hair-splitting decision that was not entirely satisfactory to many who had followed the work done on this element. The controversy was opened in 1926 by Harris, Yntema, and Hopkins, who announced the discovery of element 61 at the University of Illinois upon the basis of spectroscopic evidence obtained from concentrates of neodymium and samarium salts. They claimed to have obtained 135 lines in the arc spectrum, two bands in the absorption spectrum, and two faint X-ray lines in the *L* series, which they attributed to the presence of the rare earth element 61. On the basis of this claim of discovery they proposed that the new element be named *illinium* in honor of the University of Illinois, where the work was done. The conclusions were criticized by Prandtl, Franke, and Grimm, who were unable to duplicate the work of the Illinois group, and in their criticisms they stated that the asserted discovery must have been made upon the basis of spectral evidence from contaminating materials. The illinium claim would probably have gained little headway had it not been for the fact that W. A. Noyes, then director of the laboratories at the University of Illinois, contributed a number of articles in its defense.

Immediately after the illinium announcement Rolla and Fernandes of the Royal University of Florence, Italy, came forth with a claim for the discovery of the same element. Moreover they maintained that their work was performed prior to that of the Illinois group and that, although unpublished, their results had been placed in a sealed packet and deposited with the Academy of Lincei in 1924. In this packet they reported that their deductions were based upon X-ray and spectral absorptions of a didymium earth fraction in which the new element was supposedly concentrated. For the new element they proposed the name *florentium* in honor of the city of Florence.

In late 1926 James and Fogg of the University of New Hampshire completed a fractionation of ytterspar and sent the concentrate to J. M. Cork of the University of Michigan for X-ray analysis. Their published results indicate seven lines of the *L* series, falling between the corresponding lines for the elements 60 and 62, in the X-ray spectrogram. Such a

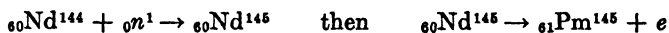
spectrogram should have constituted strong evidence to support a claim for discovery of element 61. However, their work apparently went unnoticed because of the heated arguments that were taking place between the other claimants.

In 1934 Ida Noddack reported a rather thorough investigation by X-ray analysis of various rare earth specimens in a search for element 61. Inasmuch as her results were entirely negative she suggested that the absence of element 61 in the rare earth group might be due to its instability.

In the period between 1938 and 1942 a research team at Ohio State University investigated artificial radioactivity induced by a cyclotron in the Nd-Sm region. This group, composed of H. B. Law, M. L. Pool, J. D. Kurbatov, and L. L. Quill, showed that when neodymium and praseodymium were subjected to bombardment by neutrons, protons, deuterons, and alpha particles a number of activities were obtained which might be attributed to radioisotopes of element 61. However, the assignment of these activities was made without chemical separation, and later some of them were found to be incorrect. Working with this group, C. S. Wu and E. Segrè in Berkeley, Calif., also obtained from cyclotron bombardment activities which were attributed to element 61. On the basis of their results Pool and Quill proposed the name *cyclonium* for the new element as a recognition of the essential role of the cyclotron in synthesizing new elements.

In 1947 J. A. Marinsky, L. E. Glendenin, and C. D. Coryell reported the chemical separation and identification of radioisotopes of element 61. This element appears in the fission products of uranium-235. By means of ion-exchange resin adsorption and elution technique they were able to effect the separation of tracer amounts of the new element. More recently macroquantities of the element have been prepared and separated in this fashion. The name *prometheum* was proposed by Marinsky and Glendenin after Prometheus, the Titan in Greek mythology, who stole fire from heaven for the use of mankind. The International Union of Chemistry recommended the adoption of the name *promethium*, symbol Pm, and thereby acknowledged the claim of Marinsky, Glendenin, and Coryell to the first isolation of element 61.

The first two radioisotopes of promethium to be prepared were Pm^{147} , with a half life of 3.7 years, and Pm^{149} , with a half life of 47 hours. At least 10 other isotopes have since been identified. In addition to being a fission product of uranium, promethium may also be prepared by the irradiation of neodymium with neutrons. The reaction is a two-step process in which the irradiated product undergoes beta decay to produce element 61.



8-27 Astatine. Element 85 belongs to the halogens and was sought for a long time among naturally occurring members of this family. However, the search has been a fruitless one, and all evidence now available indicates that this halogen does not occur in nature in amounts which can be determined by chemical means. The only evidence submitted for the natural occurrence of element 85 is that based upon the magnetooptic method of F. Allison. The underlying principle of this method is based upon the determination of the time lag in the Faraday effect. The latter effect is a phenomenon manifested as the rotation of the plane of polarization in light by a liquid when placed in a magnetic field. It is generally assumed that the Faraday effect does not lag behind the application of the magnetic field, but Allison maintains that there is a lag and that each chemical compound produces its characteristic minimum of light intensity. He has utilized the method for the detection of various ions in analytical chemistry, and during the period between 1929 and 1932 he and his collaborators have reported evidence of elements 85 and 87 in minerals such as lepidolite and pollucite. For element 85 Allison proposed the name *alabamine* in honor of Alabama, the state in which the work was done. The validity of the magnetooptic method of analysis has not been adequately confirmed by other scientists who have endeavored to duplicate Allison's technique.

Element 85 was first produced by D. R. Corson, K. R. Mackenzie, and E. Segrè in 1940. They synthesized the element by bombarding bismuth with high-energy alpha particles from a cyclotron. Following the precedent of naming the halogens after a Greek adjective denoting some property of the element, these workers proposed the name *astatine*, which means *unstable*, since it is the only halogen without a stable isotope. The first isotope to be obtained was At^{211} , with a half life of 7.5 hr. Its synthesis may be indicated as



At least 18 isotopes of astatine have been reported. The longest-lived of these is At^{210} with a half life of 8.3 hr.

The high specific alpha activity of astatine makes it necessary to work with the isotopes of the element in dilute solutions and in tracer quantities. It has been estimated that a molar solution would emit 10^{16} alpha particles per milliliter per second and would be sufficient to decompose the water in which the radioisotope might be dissolved. The element has physical and chemical properties that are similar to the other halogens. It is heavier than iodine and quite volatile at room temperature. Astatine has a specific affinity for metallic silver surfaces even at temperatures above 300°C . It apparently exists in aqueous solution as the free halogen from which the latter may be extracted with carbon tetrachloride

or benzene. Experiments indicate that astatine may exist in the -1 , $+1$, and $+5$ oxidation states.

8-28 Francium. In 1930 F. Allison claimed the detection of element 87 in certain samples of pollucite. Inasmuch as no other person has been able to duplicate Allison's magnetooptic method for the identification of this element, his results are regarded as speculative. Allison proposed the name *virginium*, after the state of Virginia, for this element. In 1931 Papish and Wainer at Cornell claimed to have obtained spectroscopic evidence of element 87 from a concentrate of materials obtained from 10 kg of samarskite. It is now believed that this evidence resulted from the use of a defective optical prism. K. T. Bainbridge, employing a Dempster spectrograph, has examined concentrates from pollucite and lepidolite in a search for element 87, with negative results.

In 1914 Paneth, while working with the actinium disintegration series of elements, observed that the isotope Ac^{227} , which decays mainly by beta emission, also emits some alpha particles. Since it was difficult to obtain actinium free from other radioactive substances, he could not verify this observation conclusively. It was not until 1939 that Mlle M. Perey in France was able to show that actinium-227 exhibits a branched disintegration (Sec. 8-6) with francium as the minor product. The 1.2 per cent disintegration into francium is indicated in Table 8-5. Mlle Perey proposed the name *francium* for the new element after her native country. The isotope, Fr^{223} , which she discovered, has a half life of 21 min.

At least nine other isotopes of francium have been reported. Most of these were discovered as branched-chain products in one or more of the radioactive decay series. It is interesting that Fr^{222} and Fr^{212} have been identified among spallation (Sec. 8-13) fragments resulting from the bombardment of thorium with high-speed protons.

The longest-lived isotope of francium now known has a half life of 21 min, and longer-lived isotopes are not probable. Thus francium has the dubious distinction of being the most unstable of any of the known elements. Because of its very short life, the chemistry of francium has been reduced largely to a radiochemical study of its coprecipitation behavior. Our knowledge in this respect is derived almost entirely from the researches of Mlle Perey. Her work may be summarized in the simple statement that francium shows the behavior that might be expected of the heaviest alkali metal.



RADIOACTIVE ELEMENTS AS TRACERS

The ordinary chemical elements, with few exceptions, are composed of a mixture of isotopes, and each mixture remains fairly constant in composition through the majority of physical and chemical changes. If an

isotope has a characteristic property which permits it to be identified among other isotopes of the same element, then this isotope may act as a tag or label to follow the fate of the element through a sequence of chemical or physical changes. At present only two characterizing properties are known by which isotopes may be identified among other isotopes, and they are unusual *mass* and *radioactivity*. Either of these properties may be utilized to trace the course of an element in various processes. An isotope added for this purpose is known as an *isotopic tracer*, and the element which is labeled by the particular isotope is called a *tracer element*.

It has been predicted that the large expenditures of money and materials for nuclear weapons during the World War II will be amply repaid by the variety of isotopes that have been made available through the impetus of wartime research. It is impossible to evaluate the contribution of isotopic methods to the welfare of humanity. The possibilities for the isotopic method of solving problems in science appear almost infinite. Certainly we can only touch upon small segments of this rapidly expanding field in our brief survey.

8.29 General Principles in the Use of Isotopic Tracers. An element may be labeled by changing its natural isotopic composition. Enriched stable isotopes may be used as tracers, although only a limited number of such isotopes are available for this purpose. Among those stable isotopes which are widely used for tracer studies are those of oxygen, hydrogen, carbon, nitrogen, and sulfur. Oxygen and nitrogen have no satisfactory radioactive isotopes, and the only available tracers are the heavy isotopes O^{18} and N^{15} . The choice between enriched heavy stable isotopes and radioactive isotopes for tracer studies is dependent upon the nature of the investigation and the extent to which the labeled isotope may be lost in the process. Frequently there is no choice, inasmuch as enriched heavy isotopes are limited to relatively few elements, while, on the other hand, certain elements such as oxygen and nitrogen do not have radioactive isotopes of suitable half lives for tracer methods.

As a general rule, radioisotopes are favored over stable isotopes in tracer studies because the former are more easily detected and followed through a sequence of changes. Furthermore radioisotopes are more readily available for a large number of the elements. Such isotopes are obtained from four principal sources: (1) members of one of the natural radioactive decay series; (2) irradiation of stable elements with high-speed projectiles from accelerators such as the cyclotron; (3) irradiation of stable elements with neutrons from an atomic reactor pile; and (4) the products of atomic fission. Isotopes from these sources, as well as a number of stable isotopes, are available for approved research projects from the Isotopes Division, Atomic Energy Commission, Oak Ridge, Tenn. It should be pointed out that practically all artificial isotopes

used in tracer investigations are beta emitters, and the continuous decay of these nuclides is lowering the concentration of each tracer at a constant rate. Consequently the time factor may be quite important in the practical use of such tracers. It is generally estimated that a radioisotope is effective over a period of about ten times its half life. In Table 8-10 are listed some of the most common radioactive isotopes that are used as tracers.

TABLE 8-10 COMMON RADIOISOTOPES USED AS TRACERS

<i>Isotope</i>	<i>Half life</i>	<i>Isotope</i>	<i>Half life</i>
H ³	12 years	S ³²	87.1 days
C ¹¹	21 min	Ca ⁴⁵	152 days
C ¹⁴	5,700 years	Fe ⁵⁹	46 days
N ¹³	9.9 min	Co ⁶⁰	5.3 years
O ¹⁵	125 sec	Cu ⁶⁴	12.8 hr
Na ²²	3.0 years	Br ⁸²	34 hr
Na ²⁴	14.8 hr	I ¹³¹	8.0 days
P ³²	14.3 days	Hg ²⁰³	43 days

Radioisotopes of either very short lives or very long lives are not usually suited to tracer work. The short-lived species limit the time for observation, whereas the long-lived varieties may emit such feeble radiation that it is difficult to detect. Also it should be obvious that an appreciable amount of radiation may be harmful to the observer and to any living tissues if the latter are being subjected to tracer investigations.

An isotopic tracer provides a means for the quantitative determination of a compound that may be present in a mixture of related substances. Two types of assaying instruments are used for analytical determinations. In experiments involving radioactive isotopes the measuring instrument is the electroscope, the electrometer, or the Geiger-Muller counter. The latter device contains an ionization chamber and an electronic system which perform the functions of detecting and amplifying each disintegration of an atom. The number of disintegrations and their rate serve as a measure of the amount of radioactive material that is present. In experiments using stable isotopes the measuring instrument is the mass spectrometer (Sec. 1-23). In this instrument, atoms under analysis are ionized and passed through a magnetic field. Separation is effected by differences in mass deflections. Methods for detecting radioisotopes are far more sensitive than those for isotopes with mass differences. In some cases it is possible to dilute a labeled radioactive isotope as much as 100,000 times and still be able to measure its activity in diluted samples. On the other hand, with mass isotopes such as N¹⁵ and C¹³, a dilution of as much as 500 times may render their determinations uncertain. In most cases the limits of dilution for mass determinations in tracer studies are approximately 100 times. These figures indicate that radioisotopes may

be at least 1,000 times more sensitive to detection than isotopes, depending upon mass differences.

← 9-30 **Applications of Radioisotopes to Analyses.** One of the earliest studies with radioactive tracers was that of G. Hevesy and F. Paneth, who in 1913 used natural radioactive elements to determine the solubilities of sparingly soluble salts. In determining the solubility of lead chromate they added a known quantity of a radioisotope of lead, Pb^{212} , to a definite amount of a soluble lead salt. The activity of the resulting mixture was measured, so that a relationship was established as to the activity of the material per milligram of lead. The soluble mixture of lead ions was precipitated as lead chromate and held at constant temperature until the saturated solution of the fairly insoluble material had reached equilibrium. After ascertaining the total volume of supernatant liquid, a sample of definite volume was withdrawn and evaporated to dryness. The activity of the minute residue was determined in the same fashion as upon the mixture before precipitation. From the activity of the residue it was possible to establish what weight of lead was dissolved in a known quantity of solution.

The *isotopic dilution method* is useful in analytical chemistry. An example of this method is the determination of blood volume in an animal or human being. The procedure involves the injecting of a tracer in a donor subject and allowing sufficient time for incorporation (sometimes weeks) of the tracer into the circulating red cells. A tracer that has been used for this purpose is radioactive iron, Fe^{59} . A sample is withdrawn from the donor, its activity determined per milliliter of blood, then an aliquot portion of the sample introduced into the recipient subject. After a proper elapse of time a sample from the recipient is assayed for radioactivity. From the dilution of activity it is possible to calculate the volume of blood in the recipient. Isotopes other than Fe^{59} have been used in blood-dilution investigations.

The solubility of water in benzene or other hydrocarbons is too small to be measured by ordinary physical or chemical methods. If, however, a definite quantity of radioactive tritium, H^3 , in the form of tritium oxide is added to a given amount of water, the resulting mixture has an activity that can be measured in the minute amounts that may dissolve in organic solvents.

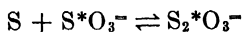
Isotopic dilution analysis is becoming increasingly important in analytical biochemistry. An example is the determination of the percentage of glycine present in the products of protein hydrolysis. By ordinary chemical methods such a determination would be quite difficult and time-consuming. In the isotopic dilution method a definite weight of synthetic glycine containing a labeled carbon atom, C^{14} , is added to a weighed quantity of the protein material. After sufficient time for mix-

ing a portion is removed from the mixture and purified as to glycine content. The sample of pure glycine so obtained is composed of a mixture of labeled and unlabeled molecules. Testing the activity of the sample indicates the amount of labeled glycine present and the extent to which the sample has been diluted by unlabeled glycine. From these values it is possible to calculate the total amount of unlabeled glycine in the original protein sample. Thus, all that is necessary to know is the labeled content of a weighed amount of the tracer added, the weight of the mixture, and the labeled content of a purified sample from the combined mixture.

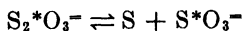
In another method of tracer analysis the sample is subjected to nuclear bombardment and then analyzed for its radioactive content. This procedure, known as *activation analysis*, is limited in its applications, and its success is dependent upon the components of the sample under analysis. In principle it should be possible to irradiate a mixture of elements so that their induced radioactivities are different. Therefore it is sometimes possible to detect very small amounts of an impurity in a sample by subjecting it to irradiation in such a manner that the impurity is selectively converted into a radioactive isotope. This technique has been developed to a point where analyses accurate within 10 per cent can be carried out for microgram quantities of certain elements. The method has been used for the analysis of mixtures of the rare earth metals and for the detection of gallium in iron, copper in nickel, and hafnium in zirconium.

8-31 Reaction Mechanisms through Tracer Chemistry. Radioactive tracers are invaluable tools for investigations involving the structure of compounds, the nature of chemical linkages, the mechanisms of chemical reactions, and the kinetics of chemical reactions. Certainly the factual knowledge of chemistry is being placed on a firmer foundation as a result of these studies. A few examples should indicate their nature and importance.

One of the first applications of tracer chemistry to structural problems was the establishment of the structure of the thiosulfate ion. If sulfur is heated with labeled sulfite ions, the thiosulfate ion may be produced according to the equation

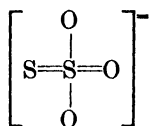


When the thiosulfate, containing a labeled sulfur atom, is broken down in an acid solution, the products are sulfur and sulfite ions:



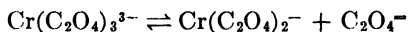
After decomposition of the thiosulfate the labeled sulfur remains linked to oxygen atoms in the sulfite ion. This clearly indicates that the bond-

ing of the labeled sulfur is unaffected in the synthesis and decomposition of the thiosulfate. It also shows that the sulfur atoms are not equivalent; otherwise the labeled isotope would have been distributed between the products of decomposition. This investigation has led to the following proposed structure for the thiosulfate:



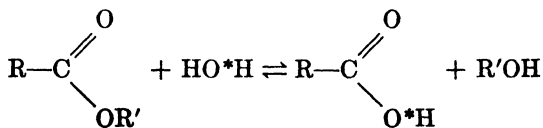
In a similar type of experiment it has been shown that the two lead atoms in lead sesquioxide, Pb_2O_3 , are not equivalent. Similar studies have been made upon various chemical combinations of ferric ions with cyanide ions.

Another example of the use of tracers in structural investigations is a study of the mechanism producing racemization in the optically active chromioxalate ion, $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$. This ion when placed in water solution is converted from an optically active ion to one that is optically inactive. The process is called *racemization*, and the inactive product is known as a *racemic form*. The racemization of the chromioxalate takes place rapidly, and it had been proposed that the reaction mechanism was one of ionization, as indicated by the equation



Another theory postulated an intramolecular rearrangement as a result of which the ion lost its optical activity. The question was settled by permitting racemization to take place in a solution containing radioactive C_2O_4^{-} (synthesized with C^{11}). It was found that no radioactivity entered into the chromium complex ion, which might be expected if the foregoing reaction were an ionic equilibrium. Thus the ionization theory was disproved, leaving the explanation for the racemization to some type of intramolecular rearrangement.

The course of certain organic reactions can be traced with labeled atoms. One profitable study has revealed the mechanism taking place in ester hydrolysis. Since oxygen does not have a radioisotope sufficiently long-lived for tracer studies, it was necessary to use the stable O^{18} isotope as the labeled atom. The hydrolysis of an ester by water enriched with heavy oxygen is indicated as



The fact that the labeled oxygen is contained in the acid proves that the OR' group has been substituted by the O*H group in the hydrolytic reaction.

8-32 Radioisotopes in Medicine. The application of tracer methods in medicine is relatively new, but, even so, much progress has been made. This application falls largely into two categories: (1) the use of tracers in diagnostic methods for localizing bodily disorders, and (2) as therapeutic agents in the treatment of certain abnormal conditions in the body. In either case the application generally results from the fact that certain elements are preferentially absorbed by definite types of tissues.

Radioactive phosphorus in the form of a phosphate is widely used in the treatment of certain blood disorders. It has a definite advantage over X rays and other therapeutic agents in the control of polycythemia vera. This is a condition in which the bone marrow produces an excess of red corpuscles. The oral ingestion of a radioactive phosphate, containing the P^{32} isotope, results in a preferential absorption of the beta-emitting isotope in the bone marrow, where it prevents the formation of excess red corpuscles. The same treatment has been used, with less success, for another abnormal blood condition known as *leukemia*, which is caused by the overproduction of white corpuscles.

Radioactive iodine has been used for a long time as a treatment for certain thyroid complaints. Stable iodine as well as radioiodine are preferentially absorbed by the thyroid gland. This fact is utilized in the treatment of hyperthyroidism, a condition where the thyroid is overactive, and in the treatment of cancer of the thyroid. Radioactive iodine apparently destroys abnormal tissues in the thyroid gland more rapidly than normal tissues and in such manner may control abnormal growths.

A tracer element may serve as a diagnostic aid, as is illustrated by the use of radioactive sodium chloride in studying obstructive vascular diseases in the extremities of the body. Normally when radioactive sodium, Na^{24} , in the form of sodium chloride is injected in the blood stream it should pass from the forearm to the foot in its maximum concentration within a half an hour. The course of the tracer can be followed by means of a Geiger-Müller tube. If the subject has impaired circulation, the time period will be longer. Moreover it may be possible to localize the general area of the restriction by means of the counter. The amount of restriction may be a determining factor between medical treatment or amputation. In a severe obstruction the counter may serve to indicate at what level amputation should be performed.

Certain labeled atoms, as, for example, radioactive iodine, are frequently absorbed preferentially by tumorous growths. This behavior has been utilized in locating brain tumors and sometimes to determine their limits of growth. In medical research, tracer studies have made

valuable contributions. By means of tracer iron it has been possible to improve methods for storing blood for transfusions. Tracer iron has been used in studying disturbances associated with pregnancy. Tracer studies indicate that the liver is primarily responsible for the manufacture of phospholipid, a fatty phosphorus compound found in blood plasma. Tracer methods also show that thyroxine, the iodine-containing amino acid that is important in the functioning of the thyroid, can be produced by muscular and intestinal tissues. By the same methods it has been learned that reserve iron within the body is stored in the mucous membrane of the intestine.

8-33 Applications of Radioisotopes in Biological Fields. The first applications of a radioactive isotope to a biological problem was made in 1923 by G. von Hevesy. At that time the only available radioisotopes were those of the heavy metals. In his first famous experiment Hevesy bathed the rootlets of young plants with solutions of lead nitrate containing a small amount of a radioactive isotope of lead, Pb^{212} . After intervals ranging from 1 hr to 2 days various parts of the plants were burned, and the amounts of lead present in each part were calculated by the amount of the active isotope in the ashes.

Since the time of Hevesy's first experiment in plant nutrition the application of radioisotopes to biological problems has expanded to a point where volumes would be required to record the many studies that have been made in this direction. A number of excellent books are available on the subject. The most successful investigations with tracer methods have been achieved in four areas: (1) a study of the dynamics of the steady state; (2) an analysis of the transport of ions across cell membranes; (3) a study of metabolic interconversions; and (4) a study of mineral metabolism. These areas will be summarized briefly.

The Dynamics of the Steady State. At one time it was supposed that ingested food was for the purpose of supplying energy to the body and to repair or replace worn-out tissue. Furthermore it was at one time believed that proteins, carbohydrates, and fats, especially the latter, were stored in the body and left undisturbed until needed. With the aid of isotopic tracers these ideas have been proved to be entirely erroneous. There is good reason to believe that a living organism contains a multiple system of balanced chemical reactions which are dynamic in nature and, therefore, in a constant state of flux. The substances of cells and tissues are constantly being built up and broken down, and there appears to be a complex balance between chemically active materials circulating within the system and those which are a part of the system. In other words, there is a constant exchange between the elements supplied in the diet and those which make up the body tissues. It is now believed that the atoms within a living organism are undergoing a continuous replacement.

Transport of Ions across Cell Membranes. Until the development of isotopic tracers it was possible to study diffusions through cellular membranes only by means of cells which were not fixed in tissues. For practical purposes such studies in mammalian organisms were limited to membranes in the corpuscles of the blood. Also, the concentration of ions necessary to observe the rate of transport through such a membrane was an unknown factor in the property being studied. The use of isotopes has added much worthwhile information concerning the movement of ions across cell boundaries, but the nature of the transport processes is still to be determined. In other words, the use of labeled ions has permitted the conclusion that their transport across cell boundaries is governed by some active mechanism that is different from ordinary physiochemical equilibrium processes. The principles which apply to ordinary osmotic processes do not necessarily apply to the passage of ions through cellular membranes. This fact is well illustrated by the ability of the cell to maintain a high internal concentration of potassium ions in the presence of a low concentration in the external fluids. Also it appears that the cell excludes sodium ions even when the extracellular concentration is quite high. These and many others ionic movements are yet to be explained.

Metabolic Interconversions. When ordinary food is introduced into the body, its carbon atoms cannot be distinguished from those which make up the body and the metabolic fate of the food cannot be followed. On the other hand, if a sugar, fatty acid, or amino acid containing labeled carbon atoms is introduced into the body, it is possible to trace these materials as they become a part of the dynamic state of the body's constituents. The tracing of a metabolic process involves two basic steps: (1) the labeling of a food, or foodlike material, which is fed to the body, and (2) the analyzing of intermediate or ultimate products that may be formed, to determine the amount, if any, of the tracer isotope present.

The mechanism of metabolism is so complex that the appearance of a labeled isotope in the final product may be misleading. This is illustrated by the fact that under certain conditions carbon dioxide may be either a waste product or one of the small molecules which may enter into the synthesis of a more complex one. If a labeled carbon atom is in the carboxyl group of the tracer compound, it may appear as labeled carbon dioxide among waste materials. On the other hand, it is possible that labeled carbon dioxide may enter into a metabolic process in such a manner that the labeled carbon atom appears in another compound. It should be noted that one of the triumphs of tracer chemistry is the discovery that carbon dioxide can enter into a number of metabolic interconversions.

The understanding of protein metabolism has been greatly advanced by

tracer methods. It is believed that proteins are built up from simple amino acids by some process which is still unknown. However, there is good evidence that both the synthesis and breakdown of proteins in living organisms are controlled by enzymes. Moreover the synthesis and breakdown are part of the metabolic pool of the body, which is in a dynamic state of equilibrium. However, if the protein system is extracted from cellular tissues, the regulating system is either damaged or destroyed and breakdown proceeds more rapidly than synthesis. The protein breakdown takes place so rapidly that the reverse process of synthesis cannot be followed by ordinary chemical methods. Only through tracer methods is it possible to exploit a protein system before it is broken down. This is usually accomplished by the addition of a labeled amino acid such as glycine to the protein extract. Any synthesis which may take place will include the tracer compound, and after a period of time the protein may be removed and assayed for tracer content.

Mineral Metabolism. The application of tracer isotopes to the study of mineral metabolism has followed at least five different lines. These may be mentioned as (1) the movement of ions across cell membranes, (2) the metabolism of bone tissues, (3) the metabolism of trace elements, (4) the metabolism of hemoglobin, and (5) the toxicology of heavy elements. These investigations have usually followed absorption, distribution, and excretion patterns through the use of tracer materials in quantities so small as not to upset normal metabolic equilibria. Among the most fruitful of these studies is that involving calcium metabolism and the part played by the intestine in the absorption and excretion of this element. Important information concerning the role of trace elements in the body has been obtained. For example, copper appears to take a part in hemoglobin formation, cobalt is present in vitamin B₁₂, and manganese and zinc seem to play important roles in the enzyme chemistry of the body.

✓**8-34 Radioisotopes in Agriculture.** The transportation of mineral nutrients from roots to leaves and subsequent redistribution within plants can be followed through the use of radioactive isotopes. Information concerning this distribution can be most easily obtained by means of *radioautography*. This form of tracer study makes use of the effect of radioactive radiations upon a photographic plate, in much the same fashion that characterized the discovery of such activity by Becquerel. Thus a radioautograph is a form of photograph which is produced by the exposure of a sensitized plate to radioactive emanations coming either from a whole plant or from sections of plant tissues. By this means it has been possible to follow the distribution of S³⁵, supplied as sulfate, in sugar beet plants. The movement of liquids in certain plants has been traced with radioactive phosphates by radioautographic evidences.

Striking information concerning the utilization of phosphates from the

soil and from various types of fertilizers has been obtained by tracer methods. The addition of radioactive P^{32} to phosphate fertilizer provides a tool to determine the extent to which a plant may select phosphates from the native soil or from an added mineral nutrient. It may also indicate at what time in the plant's life it requires added nutrients and to what extent such additions are necessary.

Long before the development of tracer techniques it was known that certain elements were necessary for plant nutrition. Among these elements are boron, cobalt, copper, manganese, zinc, and molybdenum. The quantities necessary for proper plant development are so minute that the elements have been termed *trace elements* (not to be confused with tracer elements). The use of radioisotopes has added information concerning the use and need of these elements in plant nutrition.

Many fungicides contain sulfur, and the addition of S^{35} to fruit sprays has permitted studies concerning their uses. Such studies may indicate the effectiveness of a fungicide and in some cases the damage to the fruit resulting from its application. For example, tracer techniques show that sulfur dusted on lemon fruit will penetrate the peel to a sufficient depth to cause injury to the fruit.

3-35 Industrial Applications of Radioisotopes. The growing importance of radioisotopes in technology is perhaps best indicated by the increasing number of shipments of these materials from the Oak Ridge National Laboratory. Radioisotopes were first made available from reactors of the United States in August, 1946, and during the first year there were fewer than 50 industrial users. In the 10 years following, the number increased twenty-five-fold. However, it should be pointed out that the demands for radioisotopes have not all been for the purpose of tracer studies. The radiation effect of radioactive isotopes is utilized for such purposes as the destruction of bacteria in food and drugs, the activation of chemical reactions, the polymerization of organic monomers, etc. We shall confine our discussion to the industrial applications of radioactive tracers.

The level of a liquid in a storage tank can be measured from the outside if a gamma-emitting isotope is placed on a float within the tank. Usually the float is so arranged that it moves up and down the inside of the vessel, and its position may be indicated by an outside Geiger-Müller counter at the same height. The moving-marker technique is used in the transportation of oil in cross-country pipelines to identify a change-over in shipments. The same idea is used in tracing movements of oils through the complex piping patterns of an oil refinery.

The thickness of films may be controlled by beta-emitting isotopes that serve as a part of a monitoring instrument which automatically adjusts to

differences in thickness and density. As a film emerges from rollers, it passes between a beta source and a detector. Any change in thickness will produce a corresponding change in radioactivity transmitted between the beta source and its detector. The beta gauge activates an automatic mechanism for resetting the rollers to a predetermined level for uniform film thickness. Monitoring devices of this type are used in sheet processing for such widely varying materials as steel, aluminum, plastics, paper, and cloth. Variations of thickness may run from the use of a 67-Kev beta radiation emitted by Ni^{63} to measure ink-film thicknesses on a lithographic press to that of a 1.3-Mev radiation from Co^{60} to monitor the thickness of sheet steel.

Studies involving the mechanism of friction and the effectiveness of various lubricants have been possible through the use of radioisotopes. The rate of wear in automobile piston rings may be determined by irradiating the rings in a nuclear reactor, installing them in a test engine, and measuring the accumulation of radioactive material worn from the piston rings and collected in the oil pan. Tire manufacturers have utilized the same idea by incorporating radioactive phosphorus in a plasticizer, triphenylphosphate, to produce labeled atoms in tire treads. The rate of wear on a tire may be determined by measuring the radioactivity worn from the tire and adhering to the road. These same measurements are also used to study the rate of tire wear as a function of the speed with which it is traveling under a constant load.

The uses of radioisotopes in the metallurgical industries are numerous. In the production of metals and alloys it is necessary to subject these materials to various different treatments, as, for example, annealing, quenching, cold-rolling, etc., and it is quite important to produce uniform products from these processes. By incorporating radioactive isotopes in the metals it is possible to gain an insight as to what is taking place when a metal is subjected to a particular treatment. Information of this nature is gathered most conveniently by means of radioautographs made at various stages during a treatment.

A few other industrial applications of radioisotopes may be itemized briefly. Radioautographs are replacing the use of X-ray methods in detecting internal flaws in large pieces of metals. Valuable information concerning metallic corrosion as well as inhibition of corrosion has been obtained through the aid of radioisotopes. Optimum mixing times for materials such as paint, ink, plastic products, powders, etc., may be determined by adding tagged tracer materials. Radiocarbon-14 has been used as a tracer in studying mechanisms involved in alkylation, polymerization, catalytic cracking, catalytic synthesis, as well as many other reactions of industrial importance.

EXERCISES

1. Describe the rays given off by a radioelement. How can they be detected?
2. Compare alpha, beta, and gamma rays in terms of mass, charge, and penetrating power.
3. Explain the conditions that exist in a radioactive equilibrium.
4. What is the evidence that radioactivity is a nuclear property?
5. What is meant by half-life period?
6. Explain why rates of radioactive disintegrations are given in terms of half-life periods.
7. Define and explain the radioactive displacement law.
8. How can the concentration of a component in a radioactive mixture be determined?
9. What fractional part of the radioactivity of a sample of Ra^{226} will remain after 20 years?
10. An isotope of thorium, Th^{232} , undergoes a series of disintegrations to form a stable isotope of lead, Pb^{208} , as an end product. How many alpha and beta particles are emitted in the total decay of one atom?
11. The half life of Fr^{221} is 4.8 min. Starting with 1 mg of the isotope, how much would remain after 30 min?
12. How can the approximate age of the earth be calculated from the composition of a sample of uranium ore?
13. How can the age of the earth be estimated by the process of natural radioactivity?
14. Explain how the most abundant isotope of uranium, U^{238} , can be converted into plutonium.
15. It is said that plutonium-239, with a half life of 24,000 years, is found in nature in minute traces. Account for this occurrence.
16. Describe the principle used in the cyclotron for accelerating charged particles.
17. What is the function of graphite in a nuclear reactor?
18. Account for the neutrons which are emitted when a heavy nucleus is fissioned.
19. Explain the difference between nuclear fission and nuclear fusion.
20. State the principles underlying the operation of a hydrogen bomb.
21. List the advantages and disadvantages of radioisotopes as compared with stable isotopes for purposes of tracer chemistry.
22. Practically all artificial isotopes used in tracer investigations are beta emitters. Why should this be true?
23. Why is radioactive carbon, C^{14} , rarely introduced into the human body for tracer studies?
24. Explain the tracer technique involved in exploring protein synthesis from extracts removed from living organisms.
25. Why is the use of radioactive phosphorus preferable to that of radioactive calcium in tracer studies concerning fertilizers?
26. What radioactive emanations are utilized in making radioautographs? What principles are involved in producing radioautographs?

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Index

- Abegg's conception of valency, 148
- Abegg's rule, 148, 161
- Absorption spectra, 87-89, 95-98
- Abundance of isotopes, 41-46
- Acetic acid, complex formations in, 332
 - reactions in, 331-332
 - as solvent, 291, 330-331
- Acetic acid dimer, 219
- Acid-base behavior, 277
 - relationship, to oxidation-reduction, 309-310
 - to solubility, 277
- Acid-base concepts, 275-294
 - Arrhenius, 279-280
 - Brønsted, 283-286
 - Franklin, 280-283
 - historical, 278-279
 - Lewis, 286-288
 - Usanovich, 289-290
- Acid-base reactions, in acetic acid, 331
 - in liquid ammonia, 319-320
 - in liquid hydrogen cyanide, 330
 - in liquid hydrogen sulfide, 333-334
 - in liquid sulfur dioxide, 327
 - in selenium oxychloride, 335
- Acid-base strength, 285-286, 290-294
 - in aprotic solvents, 290-291
 - in aqueous solution, 285-286, 292-294
 - effect of molecular weight, 292-293
 - of hydrated cations, 294
 - of hydro acids, 292
 - leveling effect of solvent, 290-291
 - of oxy acids, 293
 - relationship to electronegativity, 293
- Acid-base systems, 278-290
 - electron-donor-acceptor, 285-289
 - positive-negative, 289-290
 - proton-donor-acceptor, 283-286
 - solvent, 280-283
 - water-ion, 279-280
- Acids, conjugate, 283-285
 - definition, 279
 - Brønsted's, 283-285
- Acids, hydrated, 294
 - oxy-, 293
 - properties, 278
 - simple, 292
 - strength, 285-286, 290-294
 - effect of electronegativity on, 293
 - structures, 278-279, 283-285
- Actinide contraction, 385
- Actinide elements, 378-379
 - configuration, 161
 - periodic relationships, 379
 - properties, 379
- Actinium decay series, 353
- Activity in relation to electrode potential, 303
- Age, of earth, 355-356
 - of minerals, 355-356
- Alkali, definition, 278
 - solutions in liquid ammonia, 318-319
- Alloys, classification, 209
 - crystal structures, 209-214
 - formulas, 212
 - Hume-Rothery ratios, 213
 - intermetallic compounds, 212
 - properties, 214-215
- Alpha particles, characteristics, 341-342
 - charge on, 74, 341
 - emission, 341, 344-345
 - energy, 342
 - nature, 341-342
 - range, 342-343
 - scattering, 73
- Aluminum ion, acid constant, 234
 - complexes, 230-231
 - hydrated, 230-234
 - structure, 230
 - hydrolysis, 243-244
 - radius as related to acidity, 233-234
 - reactions, 243-244
- Alums, 225
- Americium, compounds, 383
 - discovery, 382-383
 - properties, 383

410 Fundamental Concepts of Inorganic Chemistry

- Ammines, isomerism, 228**
 stability, 239, 241
 structure, 228–229
- Ammonia, complexes, 241**
 liquid, reactions in, 319–324
 as solvent, 317–318
 solution of metals in, 318–319
 structure, 192
- Ammoniates, 241**
- Ammonium ion, as acid, 284**
 structure, 287
- Amphiprotic substances, 285, 316**
- Amphoteric hydroxides, 243**
 action of, with acids, 243
 with bases, 244
- Angular momentum, 93, 114**
- Anions, distortion by positive ions, 180–181, 275**
 as electron donors, 241
- Antibonding electrons, 196**
- Antiproton, characteristics, 7**
 discovery, 6
- Aprotic substances, 291**
- Aquo-cations, 230**
 acidic nature, 233–234
 hydrolysis reactions, 233, 294
- Arrhenius' theory of ionization, 279**
- Arsenic, isomers, 264**
- Association, 218, 315**
- Astatine, chemistry, 293**
 discovery, 393
 preparation, 393
- Aston's packing fraction, 36**
- Aston's spectrograph, 34**
- Atomic binding, early theories, 162–163**
- Atomic crystals, 184, 204**
- Atomic mass unit, 3**
- Atomic nuclei, 1–15**
 constituents, 2–3
 energy levels in, 20–21
 size, 16
 stability, 25–27, 875–876
- Atomic number, 18, 74, 76–79**
- Atomic orbitals, 106–108, 163–166, 191–193**
 ionic, 149–152
 tables, 146, 151
 tetrahedral, 146
- Atomic radii (*see* Radii)**
- Atomic spectra, 86–92, 95–98**
- Atomic structure, arrangement of electrons in, 105–109**
 Bohr's concept, 92–95
 Dalton's idea concerning, 28, 70
 Rutherford's model, 72–73
- Atomic volume, curve, 141**
 periodicity, 141–143
- Atomic weights, chemical, 37–38**
 constancy in nature, 41
 isotopic relations, 38
 periodicity in, 120
 physical, 37–38
 relation between scales, 38
 Rutherford's theory, 1, 72
- Atoms, types, 129–130**
- Axes of symmetry in crystals, 181**
- Azimuthal quantum number, 100–102**
- Balancing redox equations, ion-electron method, 295**
 valence-change method, 297
- Band spectra, 87**
- Base, Brønsted's definition, 283**
 conjugate, 283–284
 Lewis' concept, 286–288
 Usanovich's idea concerning, 289–290
- Basicity, periodicity, 147, 157**
 structural relations, 147
- Becquerel's discovery of radioactivity, 339**
- Berkelium, compounds, 385**
 discovery, 384
 properties, 385
- Beryllium chloride, covalency in, 163, 170**
- Beryllium ion, complexes, 246**
 hydration, 231
- Beta decay, condition for, 18**
 range of energies, 343
- Beta particles, characteristics, 342**
 charge on, 342–343
 emission, 345
 energy, 343
- Bevatron, 6**
- Binding energy, nuclear, 22–25**
 per nucleon, 23–24
- Black-body concept, 80–83**
- Black-body radiation, 80–81**
- Black-body spectrum, 81–82**
- Bloch-Sommerfeld theory of metals, 206–208**
- Body-centered cubic lattice, 179, 182–183, 206**
- Bohr's atomic theory, 92–95**
 fundamental assumptions, 92–93
 of hydrogen atom, 93–94
 limitations, 98
- Bohr's compound nucleus, 364–365**
- Boiling point, of elements, 144**
 periodicity, 144
 of water, 218
- Bond, chemical, 160**
 origin, 160
 coordinate, 228, 287

- Bond, covalent**, 168, 186–197
 dipole, 203, 215–220
 directional characteristics, 191–193
 distances, 150, 167
 electrostatic, 167
 homopolar, 203
 hydrogen, 217–219, 273
 ion-dipole, 216, 230
 ionic, 166–167
 metallic, 204, 208–209
 polar, 197–200
 semipolar, 228
- Bond energies, comparison**, 168–170
 determination, 171–176
 table, 173
- Bond type, determination**, 161, 168–170
 magnetic criterion, 234–236
- Born-Haber cycle**, 173–176
- Bragg's X-ray spectrograph**, 76
- Brillouin zones**, 207
- Brønsted definitions**, 283
- Cadmium iodide, crystal structure**, 181
- Californium, discovery**, 385
 properties, 386
- Carbon, bond energies**, 194
- Carbon dioxide, structure**, 288
- Carbon isotopes**, 42, 396
- Carbon tetrachloride, structure**, 163
- Cathode rays**, 5, 71, 75–78
- Cells, concentration**, 307
 galvanic, 300–301
- Cesium chloride, structure**, 180
- Chelate complexes, structure**, 239, 245–246
 types, 245–246
- Chelates, bidentate**, 247–249
 classification, 247
 importance, 252–253
 quadridentate, 250
 ring structure, 239, 245–247
 sexadentate, 251
 stabilities, 239
 tridentate, 249
 uses, 252–253
- Chemical atomic-weight scale**, 37–38
 basis, 38
 conversion factor, 38
- Chromic ion complexes**, 254–255
- Cis-trans isomerism, in octahedral complexes**, 256–261
 in square complexes, 227–228
- Close packing, cubic**, 205
 hexagonal, 205
 in interstitial compounds, 211
- Close packing, in metals**, 204–206
- Cobalt ion, complexes**, 226, 228–230
 structure, 228–230
- Complex formation, in acetic acid**, 332
 in liquid ammonia, 322–323
 in liquid hydrogen cyanide, 330
 in liquid hydrogen fluoride, 325
 in liquid sulfur dioxide, 328
- Complex ion, definition**, 224–225
- Complex ions, ammonia**, 226–227, 241
 anions, 238
 binding forces, 231
 calculations involving, 236
 cations, 237
 coordinate bonds, 228, 232
 cyanides, 242
 dissociation constants, 236
 electron donors, 228
 electrostatic forces between constituents, 231
 factors affecting stabilities, 231, 236–240
 halides, 241
 hydrated, 231, 233, 239
 hydroxides, 243–244
 ion-dipole bonds, 230–231
 nature, of central ion, 237
 of coordinating groups, 238
 organic, 239, 244–246
 platinum, 227
 stability, 231–238
 sulfide, 243
 thiocyanate, 242
 thiosulfate, 242
 types, 240
- Compound nucleus, Bohr's theory**, 364–365
- Compton effect**, 85–86
- Concentration cells**, 306–307
- Conjugate acids and bases**, 283–286
- Constants (see Equilibrium constants)**
- Continuous spectra**, 76
- Coordinate bond**, 228, 232, 287
- Coordinate covalence**, 228
- Coordinating groups, nature**, 238
- Coordination, fourfold**, 178
 number, 150, 177–178, 206, 226
 relation to ionic radii, 150, 177–178
 sixfold, 177
 sphere, 228
 theory, 226–229
 threefold, 178
 twofold, 178
- Coordination compound, definition**, 225
- Copper ion, ammonia complex**, 228
 cyanide complex, 242
 halides, 241

412 Fundamental Concepts of Inorganic Chemistry

- Coulomb's law, 154, 171-172, 315
- Covalent bond, atomic orbitals, 164
 - directional characteristics, 191-193
 - electron pair, 163, 187-190
 - Heitler-London theory, 187-190
 - Hund-Mulliken theory, 188, 195-197
 - hybrid orbitals, 193-194
 - nature, 187-197
 - Pauling-Slater theory, 187-193
 - polarization, 197-200
 - relationship to electronegativity, 200-202
 - strength, 190
- Covalent chlorides, 186
- Covalent compounds, 202-203
 - physical properties, 202-203
- Crystal structures, 176-183
- Crystal systems, 181
 - classification, 177-180
 - tables, 180-181
- Crystals, alloy structures, 209-213
 - classification, 209
 - ionic, 176-186
 - metallic, 204-209
 - packing in, 204-206
 - molecular, 202-203
 - packing of structural units in, 176-181
 - unit cells in, 178-180
- Curium, compounds, 384
 - discovery, 383-384
 - properties, 384
- Cyanide complexes, 242
- Cyclization, 238-239
- Cyclotron, description, 357-359
 - sketch, 358
- Dalton's atomic theory, 28, 70
- Debye unit, 315
- Deuterium, discovery, 60-61
 - exchange reactions involving, 63-67
 - separation, by diffusion, 50-53
 - by electrolysis, 60-63
- Deuterium oxide, 61-63
- Deuteron-induced reactions, 368-369
- Diammine platinumous chloride, isomerism, 228
- Diamond, properties, 184
 - structure, 184
- Dielectric constants, 271, 315
 - and dipole moments, 271, 315
 - and ionizing power, 272, 315
 - table, 315
- Dielectric effect of solvents, 272, 315
- Dipole bonds, 215-217
 - characteristics, 216
 - classification, 216-217
- Dipole moment, definition, 216
 - electric, 216
 - induced, 217
 - permanent, 197-200, 215-216
 - relationship to solubility, 271-272
 - table, 271
- Directed bonds, 191-195
 - in ammonia molecule, 193
 - in methane molecule, 194
 - in water molecule, 193, 200
- Disintegration, rate and half life, 346-348
 - tables, 351-354
 - theory, 344-345
- Disintegration constant, 347
- Disintegration series, 350-355
- Dobereiner's triads, 121
- Earth, age of, 355-356
- Einsteinium, discovery, 387
 - properties, 387
- Einstein's mass-energy equation, 362
- Electrochemical conventions, 302-303
 - examples, 302, 305
- Electrode, reference, 306
 - single, 301-302
 - types, 302
- Electrode potential, and activity, 303
 - application, 305
 - and emf, 299
 - and equilibrium constant, 301, 307-309
 - expression for, 302
 - oxidation, 299
 - sign, 303
 - standard, 299, 303
 - table, 304-305
- Electrodotic character, 309
- Electrolytes, conductance, 185-186
 - electronic structure, 166-167
 - ionization, 185
 - solid, 171-172
- Electrolytic solution pressure, 301
- Electromotive force (emf), of cells, 302-303
 - and concentration, 307
 - and free-energy change, 299
 - and temperature, 301
- Electromotive series, 301
- Electron, affinity, 168-170
 - angular momentum, 93, 100, 103, 114
 - atom ratio, 213
 - characteristics, 5
 - density, 115, 191
 - discovery, 5
 - donor-acceptor concept, 228, 286-288
 - grouping in atoms, 105-113, 161
 - magnetic moment, 102-104, 234

- Electron, rest mass, 4
 shells, 161, 164–166
 spin, 4, 163–166, 188–190
- Electronegativity, and bond type, 200–202
 evaluation, 156
 magnitude, 156
 and periodic table, 156
 relationship, to hydrogen bonding, 217
 to ionic character, 202
 tables of values, 156, 201
- Electronic spectra, 87, 95–98
- Electronic structure, ammonia complexes, 228
 ammonium ion, 287
 carbon tetrachloride, 163
 chloride ion, 198
 chlorine molecule, 163, 198
 hydrogen chloride, 199
 inert gases, 161
 iodine chloride, 199
 nitrogen atom, 193
 oxygen atom, 193
 phosphorus atom, 165
 sodium atom, 198
 sodium chloride, 167, 198
 sulfur atom, 165
 water, 193
- Electrons, antibonding, 196
 arrangement in atoms, 92, 100–101, 109, 234–236
 bonding, 196
 differentiating, 161
 diffraction, 114
 distribution, 105–112
 energy levels, 93, 106–108
 nonbonding, 196
 pairing, 163–166
 sharing, 163
 stable configuration, 160–163
 transfer, 162
 valence, 188
 wave nature, 113–114, 189
- Electrophilic character, 309
- Electrostatic bond energy, 171
- Elements, electronegativity, 156
 electronic structure, 109
 periodic table, 132
 representative, 129, 137
 transition (*see* Transition elements)
 transuranic (*see* Transuranic elements)
 types, 129–130
 (*See also* specific elements)
- Emission spectra, 87, 95–98
- Energetics of nuclear reactions, 362–364
- Energy levels, atomic, 93, 106–108
 molecular, 195–197
- Energy levels, nuclear, 20–21, 25, 344
- Energy particle, 8
- Enrichment factor, 49
- Equations, balancing, 295
- Equilibrium, oxidation-reduction, 307–309
 radioactive, 348
- Equilibrium constants, 301, 307–308
 complex ions, 236
 from electrode potentials, 307–309
- Eutectic point, 209
- Exchange forces, 19–20, 25–27, 117
- Exchange reactions, 63–67
- Exclusion principle, 105–106
- Face-centered cubic lattice, 179, 205
- Fajan's rules, 152, 167
- Faraday unit, 306
- Fermium, discovery, 387
 properties, 387–388
- Ferric ion, cyanide complex, 242
 hydrated, 234
 structure, 232
 thiocyanate complexes, 242
- Ferrocyanide ion, structure, 235
- Ferrifluoride ion, structure, 235
- Films, unimolecular, 273
- Fission, dissymmetry, 373–374
 identification of products, 373–374
 nuclear, 366, 372–376
 by fast neutrons, 373–375
 by slow neutrons, 373–375
- Fission-yield curve, 374
- Flame spectra, 85
- Fluoride ion, complex ions, 235, 242
- Forces, electrostatic, 15, 24, 150
 gravitational, 15–16
 nuclear, 15–16, 18–20, 22–27
 van der Waals, 219–220
- Francium, discovery, 394
 properties, 394
- Franklin's theory of acids and bases, 280
 283
- Free electrons, 206
- Free energy, and chemical equilibrium, 298, 307–309
 and emf, 299
 and maximum work, 298
- Free-energy change, 298, 308
- Fundamental particles, 2
- Fusion, nuclear, 367, 376–379
- Galvanic cells, 300–301
- Gamma radiation, characteristics, 343–344

414 Fundamental Concepts of Inorganic Chemistry

- Gamma radiation, emission, 344
 - range, 843
- Glide planes, 215
- Goldschmidt's values for ionic radii, 151
- Graviton, 9
- Groups in periodic table, 131
 - gradation of properties within, 157
- Half-cells, 300–301
- Half-life period, 347
- Half-reactions, 295
- Halide complex ions, 241–242
- Halides, covalent and ionic, 186
 - melting points, 184
- Halogen compounds, bond types, 184–185
 - oxy acids, 293–294
- Hardness, 184
- Heavy water, 59, 61–63
- Heisenberg uncertainty principle, 114
- Heitler-London theory, 187–190
- Helium atom, electronic structure, 168
- Hemin, 252
- Hemoglobin, 403
- Hexagonal close packing, 205
- Hole, octahedral, 211
 - tetrahedral, 211
- Homoatomic anions, 243
- Homopolar compounds, 203
- Hume-Rothery ratios, 213
- Hybrid-bond orbitals, 193–194
- Hybridization, 193–194
 - of orbitals, in ammonia, 193
 - directional characteristics, 194
- Hydrate isomerism, 255
- Hydrated ions, 230–234, 241, 276
 - acid constants, 234
 - relationship to ionic radii, 233
 - table, 234
- Hydrates, 255
- Hydrogen bond, nature, 217
 - relationship, to electronegativity, 217
 - to size, 217
 - strength, 217
 - in structure of water, 218
- Hydrogen bonding, effect on melting and boiling points, 218
 - in hydrogen fluoride, 218
 - intermolecular, 218
 - relationship to solubility, 272–273
- Hydrogen bridge, 217–219
- Hydrogen cyanide, acid-base reactions in, 330
 - complex formations in, 330
 - as solvent, 329
 - solvolysis reactions, 330
- Hydrogen electrode, 302
- Hydrogen fluoride, hydrogen bonding, 218
 - reactions in liquid, 325
 - as solvent, 324–325
- Hydrogen halides, properties, 292
 - structure, 199, 292–293
- Hydrogen isotopes, concentration and separation, 60–65
- Hydrogen molecule, 188
- Hydrogen spectrum, 89–91, 95–98
- Hydrogen sulfide, properties, 333
 - as solvent, 332–334
 - solvolysis reactions, 333–334
- Hydrogen telluride, acid strength, 292
- Hydrolysis, anions that are proton acceptors, 284–285
 - Brønsted definitions, 283
 - cations that are proton donors, 284–285
 - hydrated metal ions, 233
- Hydroxide, amphoteric, 243
 - solubility, 244
- Hydroxide ion, complexes, 243
- Indicators, titrations in nonaqueous solutions, 320
- Inert gas elements, chemical behaviors, 161
 - periodic classification, 135
 - structures, 137
- Inner complexes, 226
- Inner transition elements, abundance, 355–356, 378
 - electronic arrangements, 130, 234–236
 - properties as related to electronic structure, 130
- Intermetallic compounds, 212
- Iodide ion, complexes, 242
- Ion-electron half-reactions, conventions, 302–303
 - in electrode processes, 300–301
 - in oxidation-reduction, 295
- Ion-electron method, 298
- Ion-exchange reactions in isotopic separations, 63–67
- Ion-exchange resins, 253
- Ion polarization, factors affecting, 167, 230–231
 - relationship to bond character, 167, 230–231
- Ionic bond, characteristics, 166–167
 - formation, 162
 - nature, 162, 166–167
- Ionic charge, 182–183, 273–274
 - relationship, to hardness, 184
 - table, 184
 - to solubility, 273–274

- Ionic compounds, dissolution, 270-271**
 - electronic structure, 167
 - physical properties, 181-186
- Ionic lattices, 176-181**
- Ionic potential, 231**
- Ionic radius (see Radii)**
- Ionization, Arrhenius' theory, 279**
 - in solids, 176-181
 - in water, 279
 - of weak acids, 284
 - of weak bases, 284-285
- Ionization energy, 168**
 - and electron affinity, 168-170
 - measurement, 169-170
- Ionization potentials, 153-155**
 - factors affecting, 154-155
 - periodicity, 153-154
- Ionizing solvents, 313-317**
 - dielectric constants, 315
 - dipole moments, 315
 - properties, 313-316
- Ions, attraction, 170-173**
 - complex (see Complex ions)
 - hydration, 230
 - hydrolysis, 233, 284-285
 - negative, 167
 - positive, 153-155, 167
- Isobars, 46**
- Isomerism, cis-trans, 256-261**
 - coordination, 254
 - in coordination compounds, 253-265
 - geometrical, 256-259
 - hydrate, 255
 - ionization, 254
 - nuclear, 46
 - optical, 259-261
 - polymerization, 255
 - salt, 255-256
 - stereo, 256-261
 - structural, 256
- Isomers, nuclear, 46**
- Isotones, 46**
- Isotope concentration and separation**
 - methods, centrifugal, 59-60
 - chemical, 63-67
 - diffusion, 50-53
 - distillation, 58-59
 - electrolytic, 60-63
 - electromagnetic, 53-55
 - factors affecting separation, 48-50
 - thermal-diffusion, 55-56
- Isotope effect, 63**
- Isotopes, abundance, 42-46**
 - definition, 27, 46
 - detection and study, 30-35
 - enrichment factor, 49-50
 - of hydrogen, 50, 60-65
- Isotopes, and mass spectrograph, 30-35**
 - of oxygen, 38
 - radioactive, work with, 394-405
 - rules relating to stability, 42-46
 - separation factor, 49
 - spectral studies, 30-35
 - stable, table, 43-44
- Isotopic masses, numerical values, 43-44**
- Isotopic tracers, 47, 394-401**
- Isotopic weight, 27, 38**
-
- Joule, 299**
-
- K-electron capture, 349-350, 361-362**
- K-series absorption, 77**
- Kinetic theory, 94, 116, 269**
- Kossel's theory, 162**
- Kossel-Lewis theory, 162-163**
-
- Lanthanide contraction, effects, 141**
 - origin, 141
- Lanthanide elements, chemical properties, 161**
 - electronic configurations, 130, 161
 - periodic relationships, 130, 379
- Lanthanide series, 130, 379**
- Larmor precession, 103-104**
- Lattice energy, in alkali halides, table, 173**
 - calculation, 171-174
 - definition, 170
 - factors affecting, 171-173
 - relationship to solubility, 175, 274-275
- Lattice types, 180**
- Laue diffraction pattern, 75**
- Law of octaves, 123**
- Layer lattice, 181**
- Lead ion, complexes, 243-244**
- Lewis structures, 187**
- Lewis theory, of acids and bases, 286-288**
 - of atomic bonding, 163
- Line spectra, 86, 89-91**
-
- Madelung constant, 172**
- Magic numbers, nuclear components, 20-21**
- Magnetic behavior as related to paired and unpaired electrons, 234-236**
- Magnetic dipole moment, 189**
- Magnetic moment, explanation, 189**
 - orbital contribution, 234
 - relationship to unpaired electrons, 234
 - spin contribution, 234
 - table, 235

416 Fundamental Concepts of Inorganic Chemistry

- Magnetic properties, relationship to stereochemistry, 263
- Magnetic susceptibility, 234–235
- Magnetochemistry, 234–235
- Malleability, 215
- Mass defect, 21–22
 - calculation, 21–22
 - definition, 22
 - numerical values, 23
- Mass-energy equivalence, 362–363
- Mass number, 25
 - and stable isotopes, 42–45
 - and unstable isotopes, 372
- Mass particles, 4
- Mass spectra of elements, 34, 53–55
- Mass spectrograph, description of various instruments, 30–35
 - Aston, 34
 - Dempster, 32–33
 - Thomson, 30–31
 - results from, 30–31
 - sketches, 30–35
- Mass spectrometer, 34–35
- Mass spectrum, 35
- Mass unit, 3–4
- Mean free path, 53, 58
- Melting point, of elements, 140
 - relation to bond type, 184–185, 203
 - tables, 139, 186
- Mendeleev's periodic system, 126, 132
 - postulations, 125–128
 - predictions, 128
- Mendelevium, discovery, 388
 - properties, 388
- Mercury isotopes, concentration, 58
- Mesons, characteristics, 13–14
 - discovery, 11–13
 - in nuclear forces, 11–12
 - types, 11–14
- Metal crystals, close-packing arrangements, 204–206
- Metallic bond, characteristics, 203–209
 - electronic concept, 204–209
 - relationship to other bonds, 206–209
- Metallic character, trends in periodic table, 147
- Metallic conduction, 214
- Metallic luster, 215
- Metallic radii, 146
- Metallic state, theory, 204–209
- Metals, atomic conductivities, 214
 - atomic radii, 146
 - physical properties, 214–215
 - solutions in liquid ammonia, 318–319
 - structures, 204–206
- Mirror-image isomerism, 259–260
- Moderator, 371
- Mohs' hardness scale, 183–184
 - table, 184
- Molecular compounds, 202–203
- Molecular orbitals, 195–197
 - approach to molecular structure, 195–197
- Molecular structure, 188–197
 - molecular orbital approach, 195–196
 - valence-bond approach, 188–190
- Molecules, polar, 197–200, 314
 - degree of polarity, 197–200, 271
- Monomolecular surface layers, 273
- Moseley's law, 78–79
- Muons, characteristics, 13–14
- Neon isotopes, concentration, 31, 51
- Neptunium, compounds, 380
 - discovery, 379
 - oxidation states, 380
 - properties, 379–380
- Neptunium decay series, 353–355
 - table, 354
- Nernst equation, 306
- Neutralization reactions, in acetic acid, 331
 - in liquid ammonia, 319–320
 - in liquid hydrogen cyanide, 330
 - in liquid hydrogen sulfide, 333
 - in liquid sulfur dioxide, 327
- Neutrino, characteristics, 7–8
 - discovery, 8
 - emission, 7
- Neutron, capture, 371
 - characteristics, 10
 - component of nucleus, 2
 - discovery, 10
 - emission, 10
 - energy, 370–371
 - magnetic moment, 11
 - production, 370
 - thermal, 370–371
- Neutron-induced reactions, 370–372
- Neutron moderators, 371
- Neutron-proton ratios, 18, 25–26
- Neutrons as projectiles, 370–371
- Newland's law of octaves, 122–124
- Nickel, complexes, 238, 240
 - dimethylglyoxime, 245
- Nitrogen isotopes, 65–66
- Nobelium, discovery, 388–389
 - properties, 389
- Noble gases, structures, 161
- Nonaqueous solvents, acetic acid, 330–331
 - liquid ammonia, 317–318
 - liquid hydrogen cyanide, 329

- Nonaqueous solvents, liquid hydrogen fluoride, 324-325
 liquid phosgene, 334
 liquid sulfur dioxide, 326-327
 selenium oxychloride, 334-335
 Nuclear binding energies, calculations, 21-23
 general conclusions, 24-25
 table, 23
 Nuclear charge, 1, 74
 Nuclear composition, 2, 18-21
 Nuclear decay, 346-348
 Nuclear energy, 21-25, 362-364, 376-378
 Nuclear fission, 366, 372-376
 energy release, 376
 liquid-drop theory, 374-375
 yields, 373-374
 Nuclear forces, 15-17, 18-20, 26-27
 Nuclear fusion, 367, 376-378
 Nuclear isomers, 46
 Nuclear particles, properties, 3-4
 Nuclear projectiles, methods of producing, 357-360
 Nuclear reactions, alpha-induced, 369
 Bohr's theory, 364-365
 deuteron-induced, 368-369
 endoergic, 363
 energetics, 362-364
 exoergic, 363
 fission, 366, 372-376
 fusion, 367, 376-378
 neutron-induced, 370-372
 orbital electron capture, 361-362
 projectile-capture, 366
 projectile-capture particle-emission, 366
 projectiles for, 357-360
 proton-induced, 367-368
 spallation, 366-367
 theory, 364-365
 types, 365-367
 Nuclear shell structure, 20-21
 Nuclear stability, 25-27, 374-376
 Nuclear structure, electron-proton concept, 17
 meson theory, 11-12, 18-21
 proton-neutron concept, 18
 Nuclear transmutations, artificial, 356-378
 natural, 338-356
 Nucleon, 2
 Nucleus, energy of formation, 22-25
 forces within, 15-16
 size, 16
 stability, 25-27
 structure, 16-21
 Octahedral complexes, 178, 232, 256-259
 Octet rule, 161
 Optical isomerism, 259-261
 Orbital electron capture, 349-350, 361-362
 Orbital hybridization, 193-194
 Orbitals, atomic (*see* Atomic orbitals)
 metallic, 209
 molecular, 188-197
 Oxidation and reduction, in acid solutions, 295
 cells, 300-301
 definitions, 294-295
 equations, 295
 equilibrium constants, 307-309
 oxidation number, 296-297
 potentials, 299
 table of standard, 304-305
 relationship to acid-base behavior, 289, 309-310
 theory, 298-299
 Oxidation-reduction reactions, 295
 in liquid ammonia, 320-321
 in liquid sulfur dioxide, 327-328
 Oxidizing agent, 295
 Oxygen, isotopes, 37-38
 labeled, 395-396
 primary standard of weight, 37-38
 Packing fraction, curve, 36
 definition, 36
 whole-number rule, 35
 Pairing of electron spins, 163-166
 Paramagnetic behavior, definition, 234
 examples, 235
 Particles, subatomic, 1-15
 Pauling's theory of metals, 208-209
 Pauli's exclusion principle, 105, 189
 Periodic law, 79, 120
 Periodic properties of elements, 120, 137-157
 atomic radii, 137, 144-148
 atomic volume, 141
 chemical, 120, 147, 156-157
 density, 139
 electronegativity, 156
 ionic radii, 149-152
 ionization potentials, 153-155
 melting point, 139
 metallic character, 147
 other physical properties, 143
 predictions, 128
 valence, 148
 within groups, 147
 Periodic table, and atomic radius, 144
 and atomic volume, 141

418 Fundamental Concepts of Inorganic Chemistry

- Periodic table, based on electron configuration, 135-137
- Campbell, 137
 - electron distribution, 129-130
 - electronegativity, 156
 - extended or long form, 133-135
 - geometrical forms, 122, 129
 - historical development, 120
 - Mendeleev, 124-128, 131-133
 - Lothar Meyer, 124
 - Newland, 123
- Phosgene (liquid) as solvent, 334
- Phosphorus atom, orbitals, 165
- Photoelectric effect, 83-84
- Photon, characteristics, 2, 8
- diffraction, 8, 85-86
- Physical atomic-weight scale, 37-38
- basis, 37
 - conversion factor, 38
- Pions, characteristics, 13
- Pitchblende, 340
- Planck's constant, 83, 95
- Planck's equation, 83
- Platinum complexes, stereochemistry, 227-228, 263
- Plutonium, compounds, 382
- discovery, 380-381
 - importance, 381
 - preparation, 381
 - properties, 381-382
- Polar molecules, 197-200, 270-272
- Polarization, by cations, 167, 181, 275
- and covalency, 167
 - induced, 217
- Polonium, discovery, 340-341
- Porphyrin, 252
- Positive rays, analysis, 30-31
- Positron, characteristics, 8
- discovery, 6
 - emission, 360-361
- Potential barrier, nuclear, 363-364, 371, 377
- Potentials, determination, 299, 303
- electrode, 299
 - single, 301-302
 - standard, 299, 303
- equilibrium constants, 301-302, 307-309
- oxidation-reduction, table, 304-305
 - sign and magnitude, 303
- Precession of electron orbits, 102-103
- Precipitation reactions, liquid ammonia, 321-322
- liquid hydrogen fluoride, 325
 - liquid sulfur dioxide, 328
- Projectiles, nuclear, 357-360
- Promethium, discovery, 392
- Promethium, properties, 392
- Promotion of electrons, 195
- Properties, periodicities, 137-157
- Protium, 50
- Proton, characteristics, 8
- component of nucleus, 2, 18
 - discovery, 5, 30
 - emission, 30
- Proton acceptor, 283
- Proton donor, 283
- Proton-induced reactions, 367-368
- Prout's hypothesis, 2, 28, 121
- Pseudohalogens, 242
- Quantum mechanics, 112-117
- Quantum numbers, 99-105
- azimuthal, 100-102
 - magnetic, 102-104
 - principal, 100
 - spin, 104-105
- Quantum theory, 80-83, 84
- origin, 80
 - Planck's concept, 80-83
- Radii, atomic, 144-147
- covalent, 146
 - determination, 145
 - factors affecting, 144
 - table, 146
 - tetrahedral, 146
 - variation with atomic number, 147
- ionic, 149-152
- calculation, 150
 - and crystal structure, 176-181
 - determination, 150
 - factors affecting, 149-152
 - relationship, to coordination number, 150, 176-181
 - to positive valence, 152
 - table, 151
 - metallic, 146
- Radioactive constant, 347
- Radioactive decay, 346-348
- Radioactive decay chains, 350-355
- tables, 351-354
- Radioactive decay series, 350-355
- characteristics, 350-353
 - tables, 351-354
- Radioactive displacement laws, 345
- Radioactive elements, naturally occurring, 349
- table, 349
- Radioactive emanations, characteristics, 341-344
- ranges and half lives, 341-344
 - table, 343

- Radioactive equilibrium**, 348
- Radioactive transmutations**, artificial,
356-378
induced, 360-362
natural, 338-356
- Radioactivity**, and age of earth, 355-356
alpha, beta, and gamma rays, 341-344
artificial, 356-378
detection, 339-340
discovery, 339
K-electron capture, 349-350
natural, 338-356
positron emission, 360-361
rates of decay, 346-348
theory, 344-345
- Radioautography**, 403
- Radioelements**, 349
- Radioisotopes**, in agriculture, 403-404
applications to analyses, 397-398
in biological fields, 401-403
industrial applications, 404-405
in medicine, 400-401
naturally occurring, 349
table, 349
tracers, 394-405
- Radium**, discovery, 339
- Radius ratio**, 150, 177-181
and coordination number, 152
effects, 180-181
rules, 177-178
table, 178
- Rare-earth elements**, 130
- Reactions**, equilibrium, 307-309
exchange, 49, 63-67
half-, 295
redox, 294
- Reduction**, 294
- Representative elements**, 129, 137
- Resonance**, 190
hybrid, 191
in hydrogen molecule, 190-191
- Resonance structures**, 191
- Rhenium**, discovery, 390
- Rhombic system**, 182-183
- Ritz combination principle**, 91
- Rule**, of eight, 161-164
eliminations, 163-164
of maximum multiplicity, 192
of two, 163-166
- Rutherford's theory of atomic structure**,
1, 72
- Rydberg constant**, 90, 98
- Salt bridge**, 300
- Salts**, characteristics, 181-186
solubility, 270-271
- Salts**, true, 185-186
table, 186
- Schrödinger equation**, 115, 188
- Screening effect**, 151, 155
- Selenium oxychloride**, characteristics, 334
as solvent, 334-335
- Semipolar bond**, 228
- Separation factor of isotopes**, 49
- Shells**, electron, 106
- Silver compounds**, characteristics, 275
structures, 275
- Silver ion**, ammonia complex, 241, 310
cyanide complex, 242
halide complexes, 241-242
thiosulfate, 242
- Single-electrode potential**, 301-302
- Slow neutrons**, 370
- Sodium chloride structure**, 163, 167, 170,
179
- Sodium solubility in liquid ammonia**,
318-319
- Solid solutions**, interstitial, 211
substitutional, 211
- Solubility**, 268-278, 313-317
factors affecting, 269-277
nature, of solute, 272-275, 314-316
of solvent, 272, 313-316
temperature, 269
of liquids, 268
relationship to hydrogen bonding, 272-
274
resulting from chemical action, 275-
278
of solids, 269-270
- Solubility curves**, 269
- Solution pressure**, electrolytic, 301
- Solution process**, 269-272
- Solutions**, definition, 268
types, 268
- Solvation**, anions, 314
cations, 274, 314
definition, 175
of electrovalent HCl, 175
energy, 175, 275-277
in equations, 176, 314
extent, 175, 276
- Solvents**, acidic, 316
amphiprotic, 316
aprotic 316
basic, 316
classification, 316
dielectric effect, 272, 315
leveling effect in, 290-291
nonaqueous, 313-335
polar, 271-272, 314-315
properties of ionizing, 272, 314-315
protic, 316

420 Fundamental Concepts of Inorganic Chemistry

- Solvents, waterlike, 313-330
- Solvolytic, 277
- Solvolytic reactions, liquid ammonia, 323
 - liquid hydrogen cyanide, 330
 - liquid hydrogen fluoride, 325
 - liquid hydrogen sulfide, 334
 - liquid sulfur dioxide, 328-329
 - selenium oxychloride, 335
- Sommerfeld theory, 100
- Space lattice of crystals, 178-181
- Space quantization, 104
- Spallation, 366
- Spectra, 87-89
 - absorption, 87-89, 95-98
 - atomic, 86-99
 - band, 87
 - classification, 87-89
 - continuous, 76
 - electronic, 87, 95-98
 - emission, 87, 95-98
 - flame, 85
 - line, 86, 89-91
 - spark, 89
 - visible and X-ray, 75-76
- Spectral lines, origin, 95-98
- Spectral series, 89-91
 - of hydrogen, 89-91, 95-98
- Spin quantum number, 104-105
- Spontaneous fission, 389
- Stability ratio, 25-26, 374-375
- Standard electrode potentials, 304-305
 - application, 305-306
- Standard states, 303
- Stationary states, electronic, 92
- Stereoisomerism, 256-265
 - octahedral complexes, 256-261
 - optical isomerism, 259-261
 - square-planar complexes, 228, 261-263
 - tetrahedral complexes, 262-265
- Structure, atoms, 105-112
 - complex ions, 226-230
 - crystals, 176-181
 - ionic compounds, 176-186
 - molecules, 188-190
 - nucleus, 15-17, 20-21
 - relationship to solubility, 273-275
- Subatomic particles, 1-15
- Subgroup elements, 131
- Subshells, atomic, 106
 - definition, 106
 - energies, 106
- Subsidiary quantum numbers, 100-105
- Sulfide, complex ions, 243
- Sulfur, oxidation states, 297
- Sulfur atom, orbitals, 165
- Sulfur dioxide (liquid), acid-base reactions in, 327
- Sulfur dioxide (liquid), complex formations in, 328
- reactions in, oxidation-reduction, 327-328
 - precipitation, 328
 - solvolytic, 328-329
 - as solvent, 326-327
- Superlattices, 213
- Synchrocyclotron, 359
- Synchrotron, 359
- Tartar emetic, 249
- Technetium, compounds, 391
 - discovery, 390
 - properties, 390-391
- Telluric acid, strength, 292
- Telluric screw, 122-123
- Thiocyanate complex ions, 242
- Thionyl chloride, 328
- Thiosulfate, structure, 398-399
- Thiosulfate complex ions, 242
- Thorium, as fertile material, 374
 - radioactivity, 343
- Thorium decay series, 352
- Titration in nonaqueous solutions, 320
- Trace elements, 404
- Tracer, atoms, 395-397
 - mass, 395-396
 - methods, 395-396
 - radioactive, 394-405
 - studies, 397-405
- Tracer chemistry, reaction mechanism, 398-400
- Transition elements, characteristics, 130
 - electronic configurations, 130, 232-233
 - magnetic moments, 234-236
- Transmutations, artificial, 356-378
 - by alpha particles, 369
 - by deuterons, 368-369
 - by neutrons, 370-372
 - by protons, 367-368
- Transuranic elements, characteristics, 378-379
 - electronic configurations, 112
 - physical properties, 379
 - separation, 381-382
- Triads, 121
- Tri-iodide ion, 243
- Ultracentrifugal separation, 59-60
- Uncertainty principle, 114
- Unimolecular films, 273
 - relationship to solubility, 273
- Unit cell, classification, 183
 - definition, 178, 183

