AN INTRODUCTION
TO THE
PRINCIPLES
OF
PHYSICAL CHEMISTRY

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FROM THE STANDPOINT OF MODERN ATOMISTICS AND THERMODYNAMICS

A COURSE OF INSTRUCTION FOR STUDENTS
INTENDING TO ENTER PHYSICS OR
CHEMISTRY AS A PROFESSION

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PREFACE

As indicated by the title, the purpose of this book is to present the principles of modern physical chemistry in the form of a systematic course of instruction and training. While designed primarily for classes composed of students who purpose to become professional chemists or physicists, it is hoped that it will serve as a suitable foundational course for any class of students who wish to obtain a usable knowledge of the subject. To the student or reader who wishes merely a general or cultural familiarity with the field covered by physical chemistry the book will probably not appeal very strongly, since the subject is designedly presented in such a manner as to require the student to do a large part of the reasoning, and many portions of the book can scarcely be pursued to advantage by most beginners in the subject except under the direction of a competent instructor.

The method of presentation adopted presupposes on the part of the student a collegiate training in general or elementary chemistry and in general physics, and a training in mathematics which includes the elements of the differential and integral calculus. The author is aware that in many elementary textbooks of Physical Chemistry it is customary to avoid the use of the calculus as far as possible, frequently even with the sacrifice of accuracy and at the risk of conveying erroneous impressions concerning some of the most fundamental relationships; and in those cases where the use of the calculus seems to be unavoidable some authors have felt it incumbent upon themselves to assume a somewhat apologetic attitude and to explain that the student must take on faith "these few derivations" but that he should not allow this fact to worry him, since with the aid of the accompanying explanations and illustrations he will still be able to understand the relationships and to apply them, even though he is not in a position to appreciate clearly what is involved in their derivation. With this dilettant attitude the writer finds himself entirely out of sympathy and the literature of chemistry unfortunately abounds in illustrations of the dangers of inculcating such an attitude in the mind of the student. In the following pages the calculus has been freely employed, and while pains have been taken to explain, illustrate and emphasize the significance and physical meaning of the derived relationships, the student who is unfamiliar with the calculus will probably realize that his grasp of the subject must in many particulars be very inadequate and if he hopes to employ the laws and principles of Physical Chemistry in an intelligent and confident manner he is strongly advised to acquire the elements of the calculus before attempting to secure any special training in Physical Chemistry.

For a well-rounded introductory course in Physical Chemistry the present book will be found lacking in one very essential feature. As implied by the title, no attempt has been made to deal with the laboratory side of the subject and in the few instances where special apparatus is figured, the figure is usually merely a diagrammatic one and the discussion of the method of measurement is restricted to making clear the nature of the quantity or phenomenon under consideration. It is assumed therefore that the instructor who makes use of the present text will accompany the class-room instruction in the principles of the subject with a closely correlated laboratory course dealing with the application of these principles to specific cases and familiarizing the student with some of the more important methods of physico-chemical measurements. Some of the peculiarities in the arrangement of the text are the result of an effort to make it easier to correlate the laboratory work with the class-room work and at the same time adapt it to the exigences of semester class schedules and the necessity sometimes of making one set of apparatus serve a number of students in succession. It is for this reason, for example, that the subject of solutions is taken up before Chapters XIX and XX, which might otherwise more logically follow Chapter XI. The arrangement is one which the author has found to work well with his own classes.

Perhaps the most radical departure from the custom which under the leadership of Ostwald has prevailed heretofore in most text-books of Physical Chemistry is in connection with the manner in which atomistics and molecular kinetics are treated. Instead of considering these systems in a special chapter as interesting but unnecessary hypothetical explanations of observed facts, they are themselves in their most essential features treated as facts already established beyond the possibility of reasonable doubt, and together with thermodynamics, are made to serve as the framework for the development of the whole subject. Even in the case of thermodynamics an attempt has been made in Chapter XI to convey to the mind of the beginning student some idea of that fundamental relationship between atomistics and thermodynamics which was brought to light by the labors of Boltzmann.

In institutions where the time available for class-room work in Physical Chemistry is equivalent to five semester hours, it will usually be possible to take up in detail some of the more important thermodynamic derivations, and to facilitate this the derivations of practically all the thermodynamic equations employed in this book are given in the Appendix with the proper cross references in the body of the text. In many institutions, however, the short time available for the introductory course in Physical Chemistry makes it necessary to postpone most of the thermodynamics to more advanced courses. The arrangement of the text has been made with this state of affairs in mind and the discussion and use of the Second Law in the body of the text is largely restricted to making clear the purely energetic character of thermodynamic reasoning, so that when a relation is given as a purely thermodynamic one the student may have a proper appreciation of the very dependable character of its foundation, even though the details of all the derivations cannot be taken up in the class room. It is hoped also that the Appendix will be found useful as a convenient reference for the occasional inquiring mind which is not satisfied to take the thermodynamic equations on faith.

In many cases the development of the principles and in all cases their applications are presented in the form of problems, of which the book will be found to contain a considerable number. For some of these the author is indebted to friends and colleagues, and to other texts, especially to Noyes and Sherrill's *General Principles of Chemistry* which was made accessible to the writer through the kindness of its authors. Most of the problems, however, have been expressly prepared for this book and unless otherwise stated the numerical data given are the results of actual experiments. It is not expected that any one group of students will work all of the problems in the book. Some of them are too difficult for the beginner to solve alone and are intended to be worked out in the class room by the instructor with whatever assistance he is able to secure from the members of the class; others (such as problem 4, Chapter XX) will be found more useful in connection with advanced courses, but it is hoped that the number and variety is sufficient to make them adaptable to any class. The author will esteem it a favor if users of the text will call his attention to errors in any of these problems or in any other part of the book.

During the preparation of this book the author has sought the suggestions and criticisms of his friends in regard to many points and is glad of this opportunity to acknowledge his indebtedness to them. For permission to make use of important material before its regular publication he is indebted to the kindness of Professors R. A. Millikan, S. J. Bates, C. A. Kraus and W. D. Harkins. He has also profited by valuable criticisms received from Professors A. A. Noyes, R. C. Tolman, and R. A. Millikan, and from his colleagues and former students, Doctors D. A. MacInnes, S. J. Bates, E. B. Millard, and others. To Dr. Millard he is also indebted for valued assistance in the reading of proof.

The first 14 chapters of the book were written in 1913 and a preliminary edition of this part of the book was published in 1914. Much of the remainder of the book has also been in type since the early part of the present year and has been in use in the author's classes. This opportunity to test the book in actual class use previous to its formal publication was accorded by the publishers and has contributed materially to the detection and elimination of errors.

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INTRODUCTION

DEFINITIONS AND UNITS OF MEASUREMENT

1. Physical Chemistry.—*Physical chemistry*, sometimes called also *theoretical* or *general chemistry*, treats of the fundamental laws and principles and the important theories and systems of classification which have been formulated in order to give scientific expression to our knowledge of the physical and chemical behavior of material substances.

2. Physical Quantities and Units.—Physical quantities and units not specifically or inferentially defined in the pages of this book are assumed to be familiar to the student from his previous study of chemistry and physics. For convenience in reference, however, the definitions of the three fundamental c.g.s. units and of a few other quantities are given below. For a more complete list the student will find Guthe's *Definitions in Physics* convenient for reference.

3. The Centimeter.—The unit of length in the c.g.s. system is defined as $\frac{1}{100}$ part of a standard meter. The standard meter is a length equivalent to the distance between the defining lines on the international prototype meter at the International Bureau of Weights and Measures (at Sèvres, France) when this standard is at 0° C.

4. The Gram.—The unit of mass in the c.g.s. system is defined as $\frac{1}{1000}$ part of the standard kilogram. The standard kilogram is a mass equivalent to the mass of the international prototype kilogram at the International Bureau of Weights and Measures.

5. The Second.—The unit of time in the c.g.s. system is defined as equal to $\frac{1}{86.400}$ part of a *mean* solar day.

6. Dimensional Formulæ.—The dimensional formula of any quantity is an expression showing which of the three fundamental c.g.s. units enter into its own unit, and the dimensions, as indicated by exponents, with which they appear. Thus the dimensional equation for viscosity is

$$[\eta]=[ml^{-1}t^{-1}]$$

7. The Liter.—A liter is a unit of capacity equivalent to the volume occupied by 1 kilogram of pure water at its maximum density and under a pressure of one atmosphere. It is equivalent to 1000.027 c.c. The $\frac{1}{1000}$ part of a liter is also frequently called a "cubic centimeter" by chemists, although this terminology is, strictly speaking, incorrect, as the milli-liter is 0.0027 per cent. larger than the cubic centimeter.

8. Units of Electricity.—The *electrostatic unit of electricity* is that quantity of electricity which repels an equal quantity, at a distance of 1 cm. *in vacuo,* with a force of 1 dyne. Its dimensions are

$$[q_e]=[m^{\frac{1}{2}}l^{\frac{3}{2}}t^{-1}]$$

The *electromagnetic unit of electricity* is 3×10^{10} electrostatic units, 3×10^{10} cm. per sec. being the velocity of light in a vacuum. Its dimensions are

$$[q_m]=[m^{\frac{1}{2}}l^{\frac{1}{2}}t^{0}]$$

The *absolute coulomb* is a practical unit of electricity defined as one-tenth of the c.g.s. electromagnetic unit. The *international coulomb* is a technical unit which, as defined by the last International Conference on Electrical Units and Standards, is the quantity of electricity required to yield a deposit of 0.00111800 gram in a silver coulometer (XVI, 5) constructed and handled in a certain specified manner. According to the most recent determinations at the National Bureau of Standards the international coulomb is about 0.004 per cent. less than the absolute coulomb.

9. Units of Electrical Resistance.—The c.g.s. unit of electrical resistance in the electromagnetic system is that resistance in which heat equivalent to 1 erg is produced when one unit of electricity passes through the resistance as a steady current for 1 second. Its demensions are

$$[R]=[m^{0}lt^{-1}]$$

the same as those of velocity.

The *absolute ohm* is a practical unit of electrical resistance defined as 10^9 c.g.s. electromagnetic units. "The *international* *ohm* is the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross-sectional area, and of length of 106.300 cm."

The other electrical units are defined in terms of the two given above.

10. Dielectric Constant.—The *dielectric constant* or *specific inductive capacity* of a substance is the reciprocal of the proportionality constant in Coulomb's Law

$$f = \pm \frac{1}{K} \frac{q_1 q_2}{l^2}$$

f being the electric force acting between two charges (q_1 and q_2) of electricity 1 cm. apart. Its unit of measurement is the dielectric constant of a vacuum and its dimensions are accordingly

$$[K] = [m^0 l^0 t^0]$$

SYSTEM OF NOTATION AND REFERENCES

11. Notation.—A consistent system of notation is used throughout this book. It follows very closely the system adopted by the International Commission for the Unification of Physico-chemical Symbols, with the addition of descriptive subscripts. Letters and symbols denoting physical quantities and constants are in most instances in Italics, and letters denoting chemical substances, in Roman capitals.

12. References.—Literature references are collected at the end of each chapter and are numbered to accord with reference numbers in the text. These references are intended to cover only the most recent literature but by consulting this literature the student will find further references which will open up to him the complete literature of any topic on which he desires further information.

Cross references throughout the book are to *chapter and section* instead of to page. Thus (XVI, 2) signifies Chapter XVI, section 2; and equation (5, XX) refers to equation number 5 of Chapter XX. The student should consult the cross references whenever they occur.

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PRINCIPLES OF PHYSICAL CHEMISTRY

CHAPTER I

THE STRUCTURE OF MATTER AND THE COMPOSITION OF SUBSTANCES

1. The Rise of the Atomic Theory.[2]—The problem of the constitution of material bodies is one which has interested philosophers since the dawn of history. Some time prior to 500 B. C., the Hindu philosopher Kanada held the theory that material bodies are not continuous but are made up of very small indivisible particles, which are in a constant state of motion, flying about in all directions. This theory, known as the **atomic theory,** was also advanced about 500 B. C. by Leucippus, the founder of the Greek atomistic school, and was further developed by his pupil Democritus to whose writings we owe all of our knowledge of the beginnings of the atomistic philosophy of the Greeks. These ancient atomic theories were, however, entirely the result of purely metaphysical speculation without any experimental basis and until the birth of experimental science no further progress in this direction was possible.

The first noteworthy attempt to interpret the known behavior of material bodies in terms of the atomic theory was made in 1743 by Lomonossoff,[a] a Russian physical chemist, but his work unfortunately remained unknown outside of Russia until 1904.

[a] Michael Vassilievitch Lomonossoff (1711–1765), born of peasant parents in a little village near Archangel, became professor of chemistry in the Academy of Sciences in St. Petersburg and in 1748 built the first chemical laboratory for instruction and research. His publications stamp him as one of the greatest of physical chemists. His ideas of elements, molecules, atoms, heat, and light were essentially the same as those held today and in many ways he was so much ahead of his time that his work was ridiculed and forgotten until resurrected by Menschutkin in 1904 (See Alexander Smith, Jour. Amer. Chem. Soc., **34,** 109 (1912)).

Meanwhile in 1803, John Dalton,[a] in England, had given to the world the modern atomic theory, which has played such an important rôle in the development of the science of chemistry. Although this theory proved of the greatest assistance in the interpretation and correlation of the known facts of chemistry as well as in pointing the way toward new discoveries, it was nevertheless merely a theory, for however useful atoms and molecules, as concepts, might be in interpreting the data of science, they have, until very recently, been regarded merely as convenient hypotheses, not as actualities.

During the last decade, however, a flood of new and more refined methods of investigation has thrown a powerful light upon the old question of the structure of matter. This new evidence is, moreover, of such a striking and convincing character and comes from such a great variety of different sources that chemists and physicists of the present day may now accept the atomic and molecular structure of matter as a *fact* established beyond the possibility of reasonable doubt. Some of the more important pieces of evidence which have led to this result will be presented during the development of our subject.

2. The Structure of Matter.—Our present qualitative knowledge concerning the structure of matter and the composition of chemical substances may be briefly summed up as follows:

(*a*) **Atoms.**—Every **elementary substance** is made up of exceedingly small particles called **atoms** which are all alike and which cannot be further subdivided or broken up by **chemical processes.** It will be noted that this statement is virtually a definition of the term elementary substance and a limitation of the term **chemical process.** There are as many different **kinds of atoms** as there are **chemical elements.**

(*b*) **Molecules.**—Two or more atoms, either of the same kind or of different kinds, are, in the case of most elements, capable of uniting with one another in a definite manner to form a higher order of distinct particles called **molecules.** If the molecules of which any given material is composed are all exactly alike, the

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[a] John Dalton (1766–1844), Tutor in Mathematics and Natural Philosophy in the New College, Manchester. His New System of Chemical Philosophy appeared in 1808.

material is a **pure substance.** If they are not all alike, the material is a **mixture.**

(*c*) **Elementary Substances.**—If the atoms which compose the molecules of any pure substance are all of the same kind, the substance is, as already stated, an **elementary substance.** It is evident, however, that different elementary substances may be formed from the atoms of the same element according as the molecules which these atoms form are composed of one (monatomic molecules), two (diatomic molecules), three (triatomic molecules), or more (polyatomic molecules) atoms per molecule and even in the case of molecules composed of the same number of atoms all of the same kind, substances of different physical properties may be produced, if the atoms within the molecule are differently arranged with respect to one another. Hence the same element may exist as various different (**allotropic**) elementary substances. Thus there are several perfectly distinct substances known, each of which when allowed to unite with oxygen will produce 2 grams of pure sulphur dioxide for each gram of the substance taken. This proves that the atoms of all of these substances are sulphur atoms and the substances are all known as different forms of the element sulphur. Their different physical properties are due to differences in the internal structure or the arrangement of the molecules.

It may also happen that a given material might display nearly all of the chemical and physical properties characteristic of an element and still be composed of more than one kind of atoms. This situation has arisen recently in the case of the element lead. Richards[a] has found[8] that the atomic weight of the lead obtained from radioactive minerals is quite appreciably different (0.36 per cent.) from that of ordinary lead. The ultra violet spectra of the two materials were nevertheless found to be entirely identical, line for line, and in their chemical behavior the two "leads" were indistinguishable from each other. No separation of either material into two or more different substances could be effected and when once mixed together *not the slightest* separation of one from the other could be effected by any physical or chemical means tried. The only way in which the two

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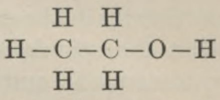
[a] Theodore W. Richards (1868–   ), Professor of Chemistry in Harvard University.

materials could be distinguished from each other at all was through their different atomic weights and through the fact that one material was radioactive (I, 2f), thus showing the presence of atoms in an unstable condition. It may be mentioned here that recent theories[6] advanced by Soddy[a] and by Fajans[b] predict the existence of groups of elements which are chemically nonseparable from one another and which differ only in the different atomic weights of the members of the group and in the different degrees of stability of their atoms. Several such groups have been studied by Soddy. It has been proposed to call the members of such a group *nonseparables* or *isotopes*. They will receive a more detailed treatment in a later chapter.[8]

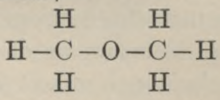
(*d*) **Compound Substances.**—If the atoms which compose the molecules of a pure chemical substance are not all of the same kind, the substance is a **compound substance.** Just as in the case of elementary substances there may be several different compound substances, all composed of molecules having the same atomic composition and owing their different properties to the different ways in which the atoms composing the molecule are arranged with respect to one another. Thus two different substances are known whose molecules are each composed of two atoms of carbon, six atoms of hydrogen, and one atom of oxygen, that is, the molecules of both substances have the composition represented by the empirical formula, C_2H_6O. The molecules of one of these substances have the structure which is represented by the formula



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ H & - & C & - & C & - & O & - & H \\ & & H & & H & & & & \end{array}$$

This substance is ordinary ethyl alcohol.

The structure of the molecules of the second substance is represented by the formula,



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ H & - & C & - & O & - & C & - & H \\ & & H & & & & H & & \end{array}$$

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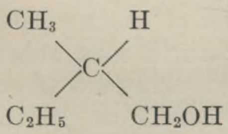
[a] Frederick Soddy, F. R. S. (1877–). Formerly Lecturer in Physical Chemistry and Radioactivity at the University of Glasgow. Since 1914 Professor of Chemistry at the University of Aberdeen.

[b] Kasimir Fajans, Investigator in the Laboratory of Physical Chemistry of the Karlsruhe Institute of Technology.

and this substance is called methyl ether. Compound substances whose molecules are identical in composition but different in structure are called **isomeric substances or isomers.**

It is obvious that the more nearly two molecular species resemble each other both in composition and in structure, the more closely will the two substances composed of these molecules resemble each other in all of their physical and chemical properties. In some cases this resemblance is exceedingly close. Thus there are two distinct substances known, both of which are called amyl alcohol and both of whose molecules have the structure represented by the formula



In nearly all of their physical and chemical properties the two substances are identical. They both have the same melting point, the same boiling point, the same heat of combustion and the same solubility in water. The chief difference between them lies in their behavior toward polarized light and this behavior serves as a means of distinguishing one from the other. If a beam of polarized light is allowed to pass through a layer of the substance in the liquid or the gaseous state, the plane of polarization is rotated to the left by one substance while the other rotates it to the right to an exactly equal degree. The first substance is called **laevo-amyl alcohol** and the second substance **dextro-amyl alcohol** for this reason. The difference in molecular structure which is the cause of this behavior is, according to the theory of van't Hoff[a]-LeBel,[b] simply a difference in the order in which the four different groups are arranged in space about the central

[a] Jacobus Henricus van't Hoff (1852–1911), Professor of Chemistry in the University of Amsterdam (1877–1896) and in the University of Berlin (1896–1911). He met Le Bel while studying with Würtz in the École de Medecine in Paris in 1874 and his paper on the asymmetry of the carbon atom appeared in September of that year. Van't Hoff is especially renowned for his contributions to the modern theory of solutions.

[b] Joseph Achille Le Bel, F. R. S., a French chemist residing in Paris.

carbon atom, the arrangements in the two cases being such that one molecule has the same arrangement as the mirror image of the other. Such isomers as these are called **optical isomers** and occur whenever a molecule is made up of four *different* atoms or groups all attached to the same central atom. The central atom under these conditions is said to be **asymmetric.**

(*e*) **Electrons.**—We have seen that the molecule of a substance is an individual composed of one or more atoms and its structure may be a very complex one, if it happens to be made up of a large number of different atoms. Modern research has demonstrated that the structure of the atom is likewise very complex. It has been shown that every atom contains a considerable number of a third and lower order of distinct particles called **electrons** or **corpuscles.** These particles seem to be nothing but free charges of **negative electricity.** They are all exactly alike, regardless of what atom they may come from, and each constitutes the smallest quantity of electricity capable of existence. In other words electricity, like matter, is atomic in structure and the electron is the "atom" of electricity. The mass (in the usual sense of this term) of an electron is not known, but some recent experiments by Tolman[a] indicate that it must be less,[9] and probably considerably less, than $\frac{1}{200}$ of the mass of the hydrogen atom, the lightest of all the atoms. The *electromagnetic mass* of an electron is known to be only $\frac{1}{1800}$ as large as the mass of the hydrogen atom. The electron is thus the smallest particle of which we have any knowledge.

(*f*) **Radioactivity.**[3]—In addition to these electrons, which seem to be part of the composition of every atom, there are also other components about which very little is known with certainty at present. All of these components are held together by the intra-atomic forces to form the complex individual system which we call the atom. The atoms of most elements are exceedingly stable and practically indestructible systems, but in some instances, especially in the case of the larger and hence probably more complex atoms such as those of the elements radium, uranium and thorium, the atomic systems, from time to time, reach a condition of instability which results in a complete break-

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[a] Richard Chase Tolman (1881-). Assistant Professor of Chemistry in the University of California.

ing up of the atom. The various components of the original atom then rearrange themselves into new atomic systems, that is, new elements are produced. This atomic disintegration may be accompanied by the violent expulsion of a stream of electrons known as **β-rays** or it may be accompanied by the expulsion of a stream of helium atoms each carrying two unit charges of positive electricity and known as **α-particles.** Such disintegrations are known as **radioactive changes** and are evidently quite distinct from **chemical reactions,** which involve the interaction of two or more atoms or molecules. All radioactive disintegrations, thus far known, are perfectly spontaneous and appear to be unaffected by any external influence which can be brought to bear upon them. They seem to be entirely determined by conditions within the core of the atom. Within recent years attempts to bring about a decomposition of certain atoms, by subjecting them to powerful electric discharges or to a bombardment by the rays given out by radium, seem to have met with some measure of success and it may eventually prove possible to break up artificially some of the elements into the simpler constituents of which their atoms are composed. There is certainly nothing in our present knowledge of the elements to justify the view that such a decomposition is impossible although it will undoubtedly be very difficult and will require the use of agencies which twenty years ago were entirely unknown to science.

(*g*) **Structure of the Atom.**—In addition to the violent expulsion of electrons which is characteristic of the β-ray disintegration in the case of radioactive elements, the atoms of all elements are able to lose temporarily or under certain special conditions a limited number of electrons without breaking up or becoming in any way unstable. In describing some of the various circumstances under which this has been observed to occur we will at the same time interpret the **known facts** in terms of an hypothesis suggested by Sir J. J. Thomson.[a] Regardless of whether this hypothesis is true or not it has the advantage possessed by all good hypotheses of serving to correlate and systematize the data

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[a] Joseph John Thomson, Kt., O. M., F. R. S. (1856–), Cavendish Professor of Experimental Physics at the University of Cambridge and Professor of Natural Philosophy at the Royal Institution, London. He is performing wonders in revealing the inner nature of the atom.

of experiment and to suggest new directions of investigation. According to the views[10] of Sir J. J. Thomson the atom is composed of a core of positive electricity containing a large number of electrons which are very firmly held. In addition to these central electrons there are a smaller number near the surface or outer shell of the atom which are very mobile and are not so firmly held. These are called **valence electrons** and their number determines the atom's maximum valency.

When one atom unites with another to form a molecule, the two atoms are supposed to be held together by an electrical attraction due either to the passage of one or more valence electrons from one atom to the other, thereby producing a *polarized molecule* with one atom charged positively and the other negatively; or due to the movements of valence electrons to or about certain positions in their own atoms, such that there is a resulting electrical attraction between the two atoms although they both remain electrically neutral since neither has gained or lost any electricity. The molecule of hydrochloric acid is, according to Sir J. J. Thomson's hypothesis, an example of a polarized molecule formed by the first method. Whether this hypothesis of the formation of the hydrochloric acid molecule be correct or not, we know that when the hydrochloric acid is dissolved in water its molecule splits up in such a way that one of the valence electrons of the hydrogen atom remains attached to the chlorine atom, which is therefore negatively charged, while the hydrogen atom which has lost the electron becomes thereby positively charged. Any free atom or molecule which carries a charge of electricity is called an **ion** and the process of the production of ions is known as **ionization.** In the case cited, the ionization of the hydrochloric acid when dissolved in water is spontaneous and is known as **electrolytic ionization** or **electrolytic dissociation.** Any substance which ionizes in this manner, that is, by solution in a suitable solvent, is called an **electrolyte.** Another type of ionization occurs when a gas is subjected to the action of the radiations given off by radium or to the action of cathode rays or various other similar agencies. The rapidly moving α- and β-particles when they collide with the atoms of the gas cause them to lose temporarily one or more of their electrons and thus to become ions. Again, when ultraviolet light is allowed to fall upon a metal it causes the metal to emit electrons and thus to acquire a positive charge. Furthermore, the electrical behavior of metals indicates that some of the electrons are able to move about from atom to atom within the body of the metal with comparative ease so that when an electromotive force is applied to the ends of a piece of metal a stream of these electrons through the metal is immediately set up. These moving electrons constitute the **electric current** in the metal.

(*h*) **Molecular Motion.**—The molecules of every substance, the atoms within the molecules and the electrons within the atoms are in constant motion. The **heat content** of any body consists of the kinetic and potential energy possessed by its moving molecules and atoms. The motion of the electrons gives rise to **radiant energy,** including light, radiant heat and Röntgen rays.

3. Hypothesis, Theory, Law and Principle.[7]—In the preceding section the value and purpose of **hypothesis** was illustrated in connection with the discussion of the structure of the atom. The terms hypothesis and **theory** are frequently used more or less synonymously but the latter term is more properly employed to designate a system which includes perhaps several related hypotheses together with all the logical consequences to which they lead, the whole serving to correlate and interpret the data of experiment in some particular field of knowledge. Thus the hypothesis that gases are composed of a large number of very small particles, together with certain auxiliary hypotheses regarding the shape, motion and energy of these particles and the forces acting between them, leads to a logical system by means of which we can interpret successfully (*i.e.*, "explain") the known facts concerning the behavior of gases. This system is called the **kinetic theory of gases.** As to the basic hypothesis that gases are *composed* of these individual particles or molecules, it has already been stated (I, 1) that the evidence supporting it has recently become so convincing that the scientific world no longer entertains a reasonable doubt of the correctness of the hypothesis. When such a condition is reached the hypothesis is considered as definitely established and is called a **fact.** There is evidently no sharp line of distinction between hypothesis and fact. It is simply a question of degree of probability. When the degree of probability of the correctness of a hypothesis becomes sufficiently high it may be regarded as a fact.

The term **law of nature** is applied to a relation, the evidence in support of which is so strong as to compel a general belief in its validity. If the relation is a very general one supported by a large and varied experience so that the chance of its ever being found invalid is extremely small it may be called a **principle.**

4. The Principle of the Conservation of Matter.—This principle states that **matter can neither be created nor destroyed. The total amount of matter in the universe remains constant.** The most exact experimental test of this principle *for a particular process* was made in 1908, by Landolt,[a] who showed, in the case of 15 different chemical reactions, that the quantity of matter (as measured by its weight) before and after the occurrence of the reaction was in every case constant to within one part in a million, which was the limit of accuracy of the experiments. The whole experience of scientists since the birth of experimental science has never yielded a single instance of an exception to this principle and its validity cannot be reasonably doubted.

5. The Law of Combining Weights.—If n_A atoms, each of mass, m_A, of the element A are united with n_B atoms each of mass, m_B, of the element B to form the molecule of a compound and if in any given quantity, M, of this compound there are n' molecules, then the total mass of the element A in the M grams of the compound will evidently be $n_A \times m_A \times n'$, that of the element B will be $n_B \times m_B \times n'$ and the ratio of the two masses will be $\frac{n_A \times m_A \times n'}{n_B \times m_B \times n'}$ or $\frac{n_A \times m_A}{n_B \times m_B}$. Since by chemical analysis or synthesis the ratio of the masses of any two elements in a chemical compound can be very accurately determined, we can in this way ascertain very exactly the numerical value of the ratio, $\frac{n_A \times m_A}{n_B \times m_B}$, which is called the **combining weight ratio** for the two elements, A and B, in this compound. If we arbitrarily agree upon some number to represent the combining weight, $n_A \times m_A$, of the ele-

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[a] Hans Landolt (1831–1910), Professor of Chemistry in the University of Berlin and founder of the Landolt-Börnstein, Physikalisch-Chemische Tabellen.

ment A in the above compound, then a value for the combining weight, $n_B \times m_B$, of the element B can evidently be readily calculated. Then by determining the combining weight ratio for a compound of a third element C with either A or B a value for the combining weight of this third element can also be calculated. Proceeding in this way we can build up a table of combining weights of all the elements capable of forming compounds and since, with the exception of the complicated molecules of certain organic compounds, the number of atoms (n_A, n_B, etc.) in any molecule is comparatively small, it is evident that the combining weights thus obtained will express accurately the relative masses of the elements which enter into chemical combination with one another in all chemical reactions. In a similar way we can show that the masses of *any* two pure chemical substances whether elements or compounds, which take part together in any chemical reaction must stand to each other in the ratio of small whole numbers, this ratio being their combining weight ratio for the chemical reaction in question.

If we arbitrarily adopt the number 8 as the combining weight of oxygen, then the **combining weight** of any other substance may be defined as that weight (in grams) of it which combines with 8 grams of oxygen; or, if the substance does not combine with oxygen, then that weight of it which combines or reacts with one combining weight of any other substance will be its combining weight. With this definition of the term, combining weight, we may state the **Law of Combining Weights** in the following terms: **Pure chemical substances react with one another only in the proportions of their combining weights.** If an element forms several compounds with oxygen it may have several combining weights. Thus in the following compounds, N_2O, NO, N_2O_3, NO_2, and N_2O_5, the number of grams of nitrogen combined with 8 grams of oxygen is 14, 7, $4\frac{2}{3}$, $3\frac{1}{2}$, and $2\frac{5}{6}$ grams respectively. Of these numbers we may, if we wish, choose any one and call it *the* combining weight of nitrogen. Thus if we choose the number 7, then the other numbers are respectively 2, $\frac{2}{3}$, $\frac{1}{2}$ and $\frac{2}{5}$ times the combining weight of nitrogen, as is required by the law of combining weights.

This law which we have here shown to be a necessary corollary of the atomic and molecular structure of matter was discovered by Richter[a] before the atomic theory was proposed by Dalton in 1808. In fact in the case of most of the laws and principles which in the following pages we shall show to be direct consequences of the atomic and molecular structure of matter, the law or principle in question was discovered empirically before the structure of matter was known and in some instances even before the modern atomic and molecular theories had been proposed. One of the triumphs of these theories was their ability to interpret all of these empirical laws from a single point of view.

Problem 1.—The following problem will illustrate the degree of accuracy with which the law of combining weights has been established: The following two sets of combining weight ratios have been determined by chemical analysis and synthesis:

(a)

$$\frac{Ag}{I}=0.849917$$

$$\frac{2\ Ag}{I_2O_5}=0.646230$$

(b)

$$\frac{LiClO_4}{LiCl}=2.5097$$

$$\frac{AgCl}{LiCl}=3.3809$$

$$\frac{Ag}{LiCl}=2.5446$$

Calculate from each set of data a value for the combining weight of silver, taking 16 as the combining weight of oxygen. (Cf. Sec. 7 below).

6. Atomic Weights.—It is evident from the preceding that if the weight of a single atom of any element is known, then the weight of an atom of any other element which combines with this one can be calculated, provided the number of atoms of each element in the molecule of the compound is known and provided the combining weight ratio of the two elements in this compound has been determined. For example, the weight of an atom of oxygen is known to be 26.39×10^{-24} grams. The molecule of water is known to consist of two atoms of hydrogen combined with one of oxygen and the combining weight ratio, $\frac{n_H\, m_H}{n_O\, m_O}$, has been found by chemical synthesis to be 0.12594. We have, therefore, $\frac{2\times m_H}{1\times 26.39\times10^{-24}}=0.12594$ and hence m_H, the weight of an atom of hydrogen, must be 16.6×10^{-25} grams. Proceeding in this way we could compute a table of the weights of the atoms of all

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[a] Jeremias Benjamin Richter (1762–1807). Chemist at the Berlin Porcelain Factory and Assessor for the Prussian Bureau of Mines. He determined the first set of equivalent weights for the metals.

elements capable of forming compounds. The practical objection to such a table is that while the *relative* weights of the atoms can be very accurately determined (to 0.01 per cent. in many cases) by chemical analysis and synthesis, the *actual* weight of any atom has not yet been determined to better than 0.2 per cent. and consequently all the values of such a table would be subject to frequent revision as our knowledge of the weight of the atom of some element became more exact. This objection can be avoided by *arbitrarily* adopting any desired number as the **atomic weight** of some one element and then computing the **relative atomic weights** of the others from their experimentally determined combining weights and a knowledge of the formula of the compound in question. Chemists have agreed to adopt the number **16** as the **atomic weight** of the element, **oxygen,** and as the basis of the **atomic weight table.**[1] In order to compute the *actual weight of any atom* from the atomic weight of the element it is only necessary to divide the latter number by

$$\frac{16}{26.39\times10^{-24}}=60.62\times10^{22},$$

the number of atoms in one atomic weight of any element. This quantity is one of the universal constants of nature and is known as **Avogadro's number.** We shall represent it by the symbol, **N.**

We have seen that if an element forms several compounds with oxygen it may have several combining weights. One of these combining weights or some submultiple of one of them will also be the atomic weight. It must evidently be that one which

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[1] The modern atomic weight table was formerly based upon the value unity which was arbitrarily taken as the atomic weight of hydrogen. On this basis the atomic weight of oxygen was found to be slightly less than 16. The atomic weights of many of the other elements were based upon combining weight ratios which involved either directly or indirectly a knowledge of the atomic weight of oxygen and this in turn was based upon the experimentally determined value of the combining weight ratio of oxygen to hydrogen. The result was that whenever new determinations resulted in a change or a more accurate knowledge of this latter ratio, it became necessary to recalculate a large part of the atomic weight table. In order to avoid this it was decided to arbitrarily adopt 16 as the atomic weight of oxygen and to employ the combining weight ratio of oxygen to hydrogen simply to determine the atomic weight of hydrogen. The atomic weights of the other elements are thus not affected by changes in the value of this ratio.

expressed in grams contains the same number of atoms as 16 grams of oxygen. Methods for deciding which of several combining weights is the atomic weight of an element will be discussed later (II, 12).

The International Committee on Atomic Weights computes each year a table of atomic weights based upon the most reliable determinations. This table is published each year in all of the leading chemical journals of the world. The International Atomic Weight Table for 1916 is given on the opposite page.

7. Chemical Formulas, Formula Weights, Equivalent Weights and Molecular Weights.—The formula of any pure chemical substance is a succession of the symbols of the elements it contains, each symbol being provided with such integers as subscripts as will make the resulting formula express the atomic proportions of the elements in the compound. In addition the symbol of each element represents one atomic weight in grams of that element and the whole formula represents a weight in grams of the substance which is equal to the sum of all the atomic weights each multiplied by its subscript. This weight is called the **gram-formula weight** of the substance. Thus the formula, HNO_3, denotes $1.008+14.01+3\times16=63.02$ grams of nitric acid and the formula, $\frac{1}{2}As_2O_3$, represents $\frac{1}{2}(2\times74.96+3\times16)=98.96$ grams of arsenic trioxide. That weight in grams of any substance which reacts chemically with one gram-atomic weight of hydrogen, or with that amount of any other substance which itself reacts with one gram-atomic weight of hydrogen, is called the **equivalent weight** or **one equivalent** of the substance. Thus the equivalent weight of each of the following substances is the gram-formula weight indicated: $\frac{1}{2}Cl_2$, $\frac{1}{4}O_2$, Ag, $\frac{1}{2}Zn$, $\frac{1}{3}Bi$, $\frac{1}{2}Ba(OH)_2$, $\frac{1}{2}H_2SO_4$, $\frac{1}{3}H_3PO_4$, $\frac{1}{3}AlCl_3$, $\frac{1}{4}K_4Fe(CN)_6$. The same substance may have more than one equivalent weight depending on whether the reaction with hydrogen is one of metathesis or of oxidation and reduction. Thus the metathetical equivalent of ferric chloride is $\frac{1}{3}$ $FeCl_3$, but its oxidation equivalent (when reduced ferrous chloride) is $FeCl_3$ and the metathetical equivalent of potassium chlorate is $KClO_3$ while its oxidation equivalent (when reduced to KCl) is $\frac{1}{6}KClO_3$.

The **molecular formula** of a substance is the formula which expresses the atomic composition of the molecule and the **molecu-**

TABLE I.—INTERNATIONAL ATOMIC WEIGHTS, 1916

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	88.7
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

lar weight (more properly, the **gram-molecular weight or the molal weight**) is the weight in grams indicated by the molecular formula. Thus the molecular formula of gaseous hydrogen, whose molecules are diatomic, is H_2 and its gram-molecular weight is $2 \times 1.008 = 2.016$ grams. The molecular formulas of some of the other elements in the gaseous state are as follows: N_2, Fe, Cl_2, Br_2, I_2, P_4, As_4, He, A, Hg, Cd, Zn. The molecular weight evidently bears the same relation to the weight of the molecule that the atomic weight does to the weight of the atom, that is, the former is in each instance **N**-times the latter. One gram molecular weight of a substance is frequently called one *mole*.

8. States of Aggregation and Phases.—Matter occurs in different states or conditions known as **states of aggregation.** The three principal states of aggregation are the **gaseous state,** the **liquid state** and the **crystalline state.** A body is said to be **isotropic** when it displays the same physical properties in all directions through it. All gases, most liquids, and the so-called amorphous solids are isotropic. **Anisotropic** bodies display different physical properties in different directions. They comprise nearly all crystalline substances. Another distinction between these two classes appears when we consider the passage of a substance from one state of aggregation to another. The passage from one isotropic state to another may be either continuous or discontinuous while the passage from the anisotropic to the isotropic state, or *vice versa,* has thus far been found to be always a discontinuous process.

Any portion of the universe which we choose to separate in thought from the rest of the universe for the purpose of considering and discussing the various changes which may occur within it under various conditions is called a **system** and the rest of the universe becomes for the time being the **surroundings** of the system. Thus, if we wish to consider the changes which occur when salt and water are brought together under various conditions of temperature, pressure, etc., then the two substances salt and water constitute our system and they are called the **components** of the system. The physically homogeneous but mechanically separable portions of a system are called its **phases.** Thus a system containing crystals of benzene, liquid benzene, and benzene vapor contains three phases, one crystalline phase, one liquid phase and one gaseous phase. If we add salt to this system we may have four phases, *i.e.*, two crystalline phases (usually called *solid* phases), namely, the salt crystals and the benzene crystals, one liquid phase composed of a solution of salt in benzene and one gaseous phase composed chiefly of benzene vapor. Each phase is distinguishable from the others by being separated from them by definite and sharp bounding surfaces and by being itself **homogeneous** throughout its own interior. By **homogeneous** is meant of uniform chemical composition throughout and having the same physical properties in all regions within itself. A system composed of only one phase is, therefore, a **homogeneous system,** while one composed of more than one phase is called a **heterogeneous system.** The distinction between phase and state of aggregation should be clearly understood. A system composed of liquid water and liquid mercury has two phases but only one state of aggregation, the liquid state. Since all gases are miscible with one another in all proportions there can never be more than one gaseous phase in any system. There may, however, be several crystalline and several liquid phases present, if the system contains a sufficient number of components. The condition, Z, of any phase of a system which has reached a state of equilibrium is ordinarily completely determined if its pressure, p, temperature, T, and composition, C, are fixed, or in mathematical language,

$$Z = \mathrm{f}\ (p, T, C) \tag{1}$$

For every heterogeneous system which has reached a state of equilibrium under a given set of conditions, there exists a relation, known as the *Phase Rule,* which connects the number (P) of phases present in the system, with the number (C) of its components and with the number (F) of variables (temperature, pressure and percentage composition of the phases) whose values must be known before the condition of the system becomes completely determined. This relation is expressed by the equation

$$\mathrm{P} + \mathrm{F} = \mathrm{C} + 2 \tag{2}$$

By C, the number of components, is meant the smallest number of substances by which the percentage composition of each phase in the system can be expressed. The derivation of the Phase Rule and a more precise definition of the quantities involved in it will be given in a later chapter.

9. Chemical Equilibrium.—When a system contains molecular species which are reacting chemically with one another to produce other molecular species which in turn are similarly constantly reacting with one another to reproduce the first ones again, so that the rates of reaction in the two directions are equal and hence the relative amounts of the different molecular species concerned remain constant, a **chemical equilibrium** is said to exist within the system. The general method for representing a chemical equilibrium will be by means of the following equation:

$$aA+bB+\ .\ .\ .\ \rightleftarrows mM+nN+\ .\ .\ .\ . \qquad (3)$$

which represents a reaction in which a molecules of the substance A, react with b molecules of the substance, B, etc., to form m molecules of the substance, M, and n molecules of the substance, N, etc., and *vice versa*.

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CHAPTER II

THE GASEOUS STATE OF AGGREGATION[1]

1. Definition and Structure of a Gas.—A substance is in the gaseous state, if it remains homogeneous and its volume increases without limit when the pressure upon it is continuously decreased and its temperature is kept constant. In gases under low pressures the molecules are so far apart and occupy such a small fraction of the total volume of the containing vessel that they are nearly independent of one another. They are in constant and very rapid motion in all directions, moving in nearly straight lines and colliding frequently with one another and with the walls of the containing vessel. They, therefore, describe zig-zag paths of such complicated and uncertain characters owing to the numerous collisions which they experience, that it is not possible to predict where a given molecule will be after an interval of time. Motion of this character is called **unordered or random motion.** The collisions between the molecules of a given gas will evidently be more frequent the greater the number of molecules in a given volume of the gas, that is, the greater the density of the gas. The average distance through which a molecule travels between two successive collisions is called the **mean free path** of the molecule. The collisions between molecules and between a molecule and the wall of the containing vessel take place without loss of energy, that is, they are **perfectly elastic** collisions. **The mean kinetic energy, $\frac{1}{2}mu^2$, of the molecules of a perfect gas has been shown experimentally to depend only upon the temperature and to be independent of the nature of the gas.** (IX, 4)

2. Boyle's Law.—The pressure (*i.e.*, the force per unit surface) exerted by a gas upon the walls of the containing vessel is due to the impacts of the rapidly moving molecules and since by definition

$$f = ma = m\frac{du}{dt} = \frac{d}{dt}(mu) \qquad (1)$$

where t signifies time, this pressure will be determined by the time rate of change of momentum, mu, which the molecules experience on striking the walls.

In order to calculate this pressure we may assume that the molecules (which in reality are constantly changing their actual velocities after each impact) are all moving with the same velocity, u, whose square is equal to the mean of the squares of the actual velocities. In other words, the velocity, u, has such a value that if all the molecules possessed it, the mean molecular kinetic energy $\frac{1}{2}mu^2$, would be unchanged. It is evident that the pressure would also be unchanged. This assumption is made for the purpose of simplifying our calculation which may, however, be carried through to the same conclusion without making this simplifying assumption. Since the pressure exerted by the gas is evidently independent of the shape of the vessel containing it, we shall assume for convenience that it is contained in a cube of side, l, and we shall consider the three components of the velocity, u, which are respectively perpendicular to the faces of the cube and are, therefore, connected with the velocity, u, by the relation,

$$u_1^2+u_2^2+u_3^2=u^2 \tag{2}$$

A molecule of mass, m, approaches face, 1, with the momentum, mu_1, perpendicular to this face and after the impact it recedes from it with the momentum, $-mu_1$, the change in momentum being, therefore, $2mu_1$. The number of impacts in unit time will evidently be $\frac{u_1}{2l}$ and the total change of momentum per unit time will be the product of the number of impacts into the change of momentum per impact, or $2mu_1\times\frac{u_1}{2l} = \frac{mu_1^2}{l}$. Similarly in the other two directions the total change in momentum on each face will be $\frac{mu_2^2}{l}$ and $\frac{mu_3^2}{l}$ respectively, and the total effect of this molecule upon all six walls of the cube will therefore be

$$\frac{2m}{l}(u_1^2+u_2^2+u_3^2)=\frac{2mu^2}{l} \tag{3}$$

If there are n molecules of gas in the cube, the total force exerted by the gas upon all the walls of the cube will be $\frac{2nmu^2}{l}$ and the force per unit area or the pressure will be

$$p=\frac{2nmu^2}{l}\div 6l^2=\frac{nmu^2}{3l^3}=\frac{nmu^2}{3v} \quad \text{or } pv=\tfrac{1}{3}nmu^2 \tag{4}$$

where v is the volume in which the molecules are free to move, here assumed equal to the volume of the cube.

Since at constant temperature the mean kinetic energy and hence mu^2 is a constant (II, 1) it follows from equation (4) that

$$pv=const. \tag{5}$$

for a given mass of any gas in which n does not change with p. This is Boyle's or Mariotte's Law. It was discovered empirically by Robert Boyle[a] in 1662 and by Mariotte[b] in 1679.

3. Gay Lussac's Law of Temperature Effect.—Equation (4) may be written

$$pv=\tfrac{2}{3}n\ (\tfrac{1}{2}mu^2) \tag{6}$$

and since the mean kinetic energies of the molecules of all gases are identical at the same temperature, it follows that the rate of change of the kinetic energy with the temperature must also be the same for all gases, for otherwise if the mean kinetic energies of several gases were all equal at one temperature, they could not be so at another. In mathematical language this statement is expressed thus,

$$\frac{\mathrm{d}(\frac{1}{2}mu^2)}{\mathrm{d}\theta}=const. \text{ (for all gases)} \tag{7}$$

where θ is the temperature. Differentiating equation (6) above we obtain

$$\frac{\mathrm{d}(pv)}{\mathrm{d}\theta} = \tfrac{2}{3}n\left(\frac{\mathrm{d}(\frac{1}{2}mu^2)}{\mathrm{d}\theta}\right) + \tfrac{2}{3}(\tfrac{1}{2}mu^2)\left(\frac{\mathrm{d}n}{\mathrm{d}\theta}\right) \tag{8}$$

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[a] Robert Boyle (1627–1691). Seventh son and fourteenth child of Richard Boyle, first Earl of Cork. Educated at Eton and on the Continent. Settled in Oxford where he erected a laboratory. One of the founders of the Royal Society of London. A man of insatiable curiosity concerning all kinds of natural phenomena.

[b] Edme Mariotte (1620–1684). The father of experimental physics in France. His treatise on *The Flow of Water and Other Liquids* appeared in 1686. His collected works were published in Leyden in 1717 and at the Hague in 1740. He was one of the earliest members of the French Academy of Sciences.

Combining this with equation (7) we have

$$\frac{\mathrm{d}(pv)}{\mathrm{d}\theta}=n\times const.+const.\times\frac{\mathrm{d}n}{\mathrm{d}\theta} \tag{9}$$

If n is a constant with respect to variations in θ, this relation becomes

$$\frac{\mathrm{d}(pv)}{\mathrm{d}\theta}=const.=k \tag{10}$$

where k is a constant independent of the nature of the gas and dependent only on the initial value of the pressure volume product. This result may be stated in words as follows: **The temperature rate of change of the pressure-volume product is the same for all gases whose molecular complexity does not change with the temperature.** This law was discovered empirically by Gay Lussac[a] in 1802. It may be expressed more elegantly and concisely by the differential equation

$$\frac{\mathrm{d}^2(pv)}{\mathrm{d}\theta^2}=0 \tag{11}$$

of which equation (10) is the first integral.

4. The Law of Avogadro.—Equation (6) may be written

$$n=\tfrac{3}{2}\frac{pv}{(\frac{1}{2}mu^2)} \tag{12}$$

from which it follows that if p, v, and $\frac{1}{2}mu^2$, and hence also θ are all constants, n is likewise a constant and has the same value for all gases; or in other words that **equal volumes of all gases at the same temperature and pressure contain the same number of molecules.** This statement, advanced as a hypothesis in 1811 by the Italian physicist Avogadro,[b] is of great importance in the determination of the molecular weights of gases. The

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[a] Louis Joseph Gay-Lussac (1778–1850). Studied in the Ecole Polytechnique at Paris under Berthollet and Laplace in 1797. His papers on the properties of gases appeared 1801–1808. He was the discoverer of cyanogen and the inventor of many accurate methods of chemical analysis.

[b] Amedeo Avogadro (1776–1856). Studied law and became a practising lawyer. In 1800 began the study of mathematics and became Professor of Physics at Vercelli and later at Turin. Avogadro's hypothesis although published in 1811 began to find acceptance among chemists only after 1860, and as late as 1885, French chemists still refused to accept it as the logical basis for determining molecular formulas.

molecule of oxygen is known to have the formula O_2 and hence the molecular weight, $2 \times 16 = 32$. Avogadro's number, the number of molecules in 32 grams of oxygen, is $\mathbf{N} = 60.62 \times 10^{22}$ as stated in the first chapter. According to Avogadro's law this is also evidently the number of molecules in one gram-molecular weight of *any* gas and the gram-molecular weight of any gas must, therefore, be, according to Avogadro's law, that mass in grams of the gas which occupies the same volume as do 32 grams of oxygen at the same temperature and pressure.

If in equation 10 of the preceding section we agree always to take one gram-molecular weight of a gas, then by Avogadro's law we have for every gas

$$\frac{\mathrm{d}(pv_0)}{\mathrm{d}\theta} = R \tag{13}$$

where v_0 is the volume of one mole of the gas and R is a constant whose value is the same for all gases. The product, pv_0, has the dimensions of force × distance and hence of work or energy. (Problem: Demonstrate this.) It represents the work required to produce the volume, v_0, against the constant pressure, p, and may be called the **molal volume energy** of the gas and the significance of equation (13) may be expressed in the following words: **The temperature rate of change of the molal volume energy has the same value for all pure gases.**

5. Definition of the Centigrade Degree and of Absolute Temperature.—The **centigrade degree** is arbitrarily defined as $\frac{1}{100}$ part of the temperature interval between the temperature of ice, melting under the pressure of one atmosphere, and the temperature of the vapor of water, boiling under the pressure of one atmosphere. The size of this degree will depend somewhat upon the nature of the material composing the thermometer employed in measuring this temperature interval. Thus on the international hydrogen scale the centigrade degree is defined as that difference in temperature which produces in the pressure of a quantity of hydrogen gas $\frac{1}{100}$ part of the change in pressure which is produced when the volume of the gas is kept constant and its temperature is changed from that of ice melting under a pressure of one atmosphere to that of the vapor of water boiling under a pressure of one atmosphere, it being further stipulated that the hydrogen shall be under a pressure of 1 meter of mercury when it is at the temperature of melting ice. If nitrogen be employed instead of hydrogen, the centigrade degree defined in a similar manner is almost identical with that of the hydrogen scale and as the initial pressure of the gas employed is decreased, the size of the degree as defined above reaches a limiting value which is entirely independent of the nature of the gas employed in the thermometer. This degree defines a temperature scale known as the Kelvin[a] or Thermodynamic Scale and may be regarded as the degree given by a thermometer filled with a perfect gas (II, 7 and 9). The degree on the Kelvin scale differs from that on the international hydrogen scale by less than 0.1 per cent. so that in nearly all cases the two scales may be regarded as identical for practical purposes. Strictly, however, we shall understand in what follows, that the centigrade degree is that defined by the Kelvin scale.

Equation (10) may be written, $d(pv)=kd\theta$ and on integration gives

$$pv=k\theta+kk'=k(\theta+k') \qquad (14)$$

where kk' is the integration constant. In other words this equation implies that the pressure-volume product of a given mass of gas is proportional to the temperature-plus-a-constant, k'. The numerical value of this constant depends upon the size of the degree on our temperature scale. If we adopt the centigrade degree as defined above, then we find by experiment with different gases that the constant k' has the value **273.1** centigrade degrees. Equation (14) may, therefore, be written

$$pv=k(t+273.1) \qquad (15)$$

and the symbol, t, will henceforth be understood to signify temperature on the *centigrade scale.*

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[a] William Thomson, Lord Kelvin (1824–1907). Studied at the Universities of Glasgow (1834) and Cambridge (1841). Professor of Natural Philosophy at Glasgow, 1846. Laid the first Atlantic cables (1857). Knighted in 1866 and created Baron Kelvin of Largs, 1892. Buried in Westminster Abbey.

The quantity, $t+273.1$, is called the **absolute temperature** and is represented by the letter T. The **absolute scale** evidently differs from the centigrade scale only in having its zero point 273.1° below the centigrade zero. Equation (15) may now be written

$$pv=kT \tag{16}$$

or in words, the **pressure volume product of a given mass of any gas is proportional to its absolute temperature.** If we differentiate this equation with respect to T and divide the result by the original equation, we have

$$\frac{1}{pv}\,\frac{\mathrm{d}(pv)}{\mathrm{d}T}=\frac{1}{T} \tag{17}$$

or stated in words, the pressure volume product (or the pressure at constant volume or the volume at constant pressure) of any gas increases by one Tth part of itself for each rise of one degree in its temperature, T being the initial absolute temperature of the gas; or, since p, v and T in the above equation may have any values, this equation also states that the increase in the pressure-volume product of a given mass of any gas per degree rise in temperature is equal to $\frac{1}{273\cdot 1}$ of its value at 0° C. These statements comprise what is frequently referred to as the law of Charles.[a]

All of these statements are evidently much more elegantly and concisely expressed by equation (11) from which we have deduced them. In fact one of the great advantages of the language of the mathematician is the clear, concise, complete and exact character of its statements. The simple statement that

$$\frac{\mathrm{d}^2(pv)}{\mathrm{d}t^2}=0 \tag{18}$$

conveys to the mind of the mathematician nearly everything which we have employed three pages in explaining. Because of these manifest advantages of the language and methods of

[a] Jacques Alexandre César Charles (1746–1823). French mathematician and physicist, Professor of Physics at the Conservatoire des Arts et Metiers. He was the first to employ hydrogen for the inflation of ballons. In 1787 he anticipated Gay Lussac's law of the expansion of gases.

the mathematician we shall use them freely throughout this book at the same time translating them, wherever desirable, into more familiar forms of statement. It is hoped that this dual method of treatment will aid the student in gaining a clearer insight into the general laws and principles of his science as well as giving him a better appreciation of the value of higher mathematics to the chemist than he may perhaps have obtained in his college courses in mathematics.

6. Dalton's Law of Partial Pressures.—In a mixture of gases we have more than one species of molecule and the total pressure exerted by the mixture upon the walls of the containing vessel may be considered as the sum of all the separate partial pressures due to the impacts of the molecules of the different gases. That is

$$p=p_{\mathrm{A}}+p_{\mathrm{B}}+p_{\mathrm{C}}+\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \qquad (19)$$

By employing the same method of reasoning used in section 2 above we can readily show that these partial pressures are each expressed by an equation of the same form as equation (4), thus

$$p_{\mathrm{A}}v=\tfrac{1}{3}n_{\mathrm{A}}m_{\mathrm{A}}u^2{}_{\mathrm{A}} \qquad (20)$$
$$p_{\mathrm{B}}v=\tfrac{1}{3}n_{\mathrm{B}}m_{\mathrm{B}}\,u^2{}_{\mathrm{B}} \qquad (21)$$
$$p_{\mathrm{C}}v=\tfrac{1}{3}n_{\mathrm{C}}m_{\mathrm{C}}u^2{}_{\mathrm{C}},\ \text{etc.,} \qquad (22)$$

or stated in words: **In a mixture of gases each gas exerts the same pressure as it would exert if it were alone present in the volume occupied by the mixture.** This statement is known as **Dalton's Law of Partial Pressures.**

Problem 1.—Show that the partial pressure, p_{A}, of any constituent A of a gaseous mixture is given by the relation

$$p_{\mathrm{A}}=\frac{n_{\mathrm{A}}}{n}p \qquad (23)$$

where n_{A} is the number of molecules of A and n is the total number of all molecules present, p being the total pressure of the mixture. Show also that the **molecular fraction,** $\frac{n_{\mathrm{A}}}{n}$, must also be equal to the number of gram molecular weights of the constituent, A, divided by the sum of the numbers of gram molecular weights of all the gases present in the mixture.

This latter ratio is called the **mole-fraction** of the constituent in question and is represented by the letter, x. Equation (23) may, therefore, be written,

$$p_A = x_A p \tag{24}$$

and similarly for another constituent of the mixture

$$p_B = x_B p \tag{25}$$

and so on for each gas present in the mixture. Stated in words: The partial pressure of any gas in a mixture is equal to its mole-fraction in the mixture multiplied by the total pressure of the mixture.

If a closed palladium vessel or tube connected with a manometer be evacuated and then placed in a gaseous mixture at high temperature containing hydrogen, the hydrogen will diffuse through the palladium wall into the vessel and will register on the manometer its partial pressure in the mixture. The palladium is impermeable to the other gases but easily permeable to hydrogen which passes through it, until its partial pressures on the two sides of the wall become the same. This device gives us a means of demonstrating by direct experiment and of measuring the partial pressure exerted by the molecules of one gas in a mixture of several gases.

7. The Equation of State of a Perfect Gas.—The laws which we have just derived, known as the **perfect gas laws,** may be conveniently combined into a single expression. To do this we have only to modify slightly equation (16) above. The numerical value of the proportionality constant, k, of this expression depends both upon the mass of gas taken and upon the nature of the gas, but if we agree that the mass taken shall always be one gram molecular weight (called also one **mole**) in every instance, then by Avogadro's law (II, 4) the value of $\frac{pv}{T}$ is the same for all gases, that is,

$$\frac{pv_0}{T} = R \tag{26}$$

where R is a universal constant which is independent of the nature of the gas and v_0 is by our agreement the volume of one gram molecular weight or one mole of the gas. It is called the **molal**

volume of the gas. If we wish to extend this equation to apply to any quantity of a gas, we have only to multiply both sides by N, the number of moles taken, and we have

$$pv = NRT \tag{27}$$

where v, the total volume occupied by the N moles of gas, is written for Nv_0. This expression is the **equation of state of a perfect gas** or more briefly the **perfect gas law.** In this equation p, v, and T denote respectively the pressure, volume and absolute temperature of the gas while N, the number of moles present, is evidently equal to $\frac{m}{M}$ where m is the mass of the gas and M its molecular weight. R is a constant, the same for all gases, and equal to the value of $\frac{pv}{T}$ for one mole of any perfect gas. Its numerical value obviously depends upon the units in which pv is expressed. If p is expressed in atmospheres and v in liters, R has the value **0.08207** liter-atmospheres per degree; if p is expressed in dynes per square centimeter and v in cubic centimeters, then R has the value $\mathbf{8.3162 \times 10^7}$ ergs or **8.3162** joules per degree; while if pv is expressed in calories, then R has the value **1.9852** calories per degree.

8. Temperature and Molecular Kinetic Energy.—It has already been stated (II, 1) that experiments have shown that the mean kinetic energy of the molecules of a perfect gas is dependent only upon the temperature. The nature of the dependence can be deduced by combining equation (4) with equation (27) so as to eliminate pv. This gives

$$\tfrac{1}{3}\, nmu^2 = NRT \tag{28}$$

or

$$\tfrac{1}{2}mu^2 = \tfrac{3}{2}\,\frac{N}{n}\,RT = \tfrac{3}{2}\,\frac{RT}{\mathbf{N}} = \epsilon T \tag{29}$$

where $\mathbf{N}$ is Avogadro's number and ϵ is evidently a constant. Stated in words: **The mean kinetic energy of the molecules of a perfect gas is proportional to the absolute temperature of the gas and the proportionality constant is equal to** $\tfrac{3}{2}\,\frac{R}{\mathbf{N}}$.

Problem 2.—From the value of R and the atomic weights required calculate the molecular velocity, u, in miles per second for the following gases:

H_2 at 0°; H_2 at 3000°; O_2 at 0°; C_6H_6 at 0°; Hg at 0°. (First eliminate **N** and m from equation (29) by introducing the molecular weight, M, of the gas.)

9. The Validity of the Perfect Gas Laws.—It will be remembered that the derivation given above for the perfect gas law is based upon equation (4) which was itself derived on the assumptions (1) that the molecules of a gas are so far apart that they exert no attraction upon one another; and (2) that the space which they themselves actually occupy is negligibly small in comparison with the volume of the containing vessel. No real gas exactly fulfills either of these conditions, but it is evident that all gases should approach these conditions more closely the lower the pressure, that is, the farther apart the molecules become. The perfect gas law, therefore, is, strictly speaking, only a limiting law which may be considered as holding exactly only for an imaginary gas, called a perfect gas, but which all real gases should obey more and more closely the lower the pressure. Experiment shows that this is actually the case. The magnitude of the divergence of real gases from the requirements of the perfect gas law varies with the nature of the gas and its temperature, but for pressures not greatly in excess of one atmosphere the divergence is small (less than 1 per cent.) for gases at temperatures far removed from their maximum condensation temperature. This is illustrated by the data in the first half of Tables II and III. The figures given in the third column are the critical temperatures of the gases. The **critical temperature,** or the maximum condensation temperature of a gas, is the highest temperature at which the gas can be liquefied by increase of pressure.

At higher pressures and at lower temperatures all gases deviate more and more from the requirements of the perfect gas law. The behavior of carbon dioxide ($t_c = 31.35°$) toward Boyle's law at various temperatures is shown graphically in Figs. 1 and 2. The way in which the *pv*-product varies with the pressure at the temperatures indicated is shown by the curves. Fig. 2 is on a larger scale than Fig. 1. The general behavior of carbon dioxide as indicated by these diagrams is characteristic of all gases.

Problem 3.—Discuss the relations displayed graphically in Figs. 1 and 2, stating in words all the relations represented by these curves.

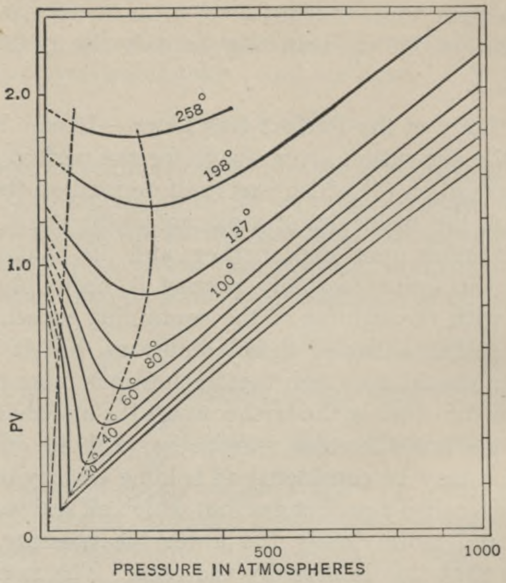

Fig. 1.

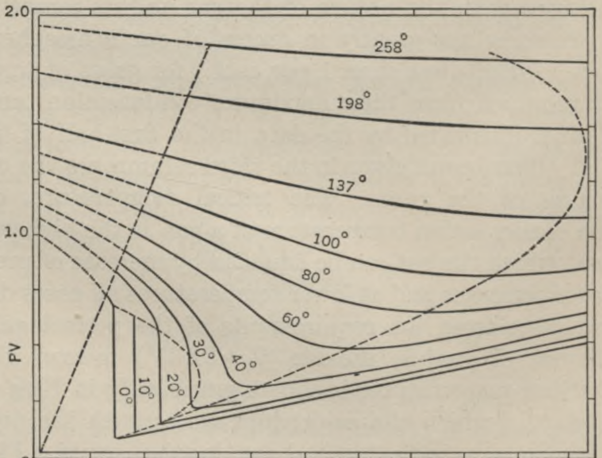

Fig. 2.

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(From Young's *Stoichiometry*.)

Table II

Values of $\frac{pv_0}{RT}$ for various gases. Illustrating the magnitude of the deviations of gases from the perfect gas law and from Berthelot's equation of state. For a perfect gas $\frac{pv_0}{RT} = 1$.

Gas	Mol. wt., M	Critical temperature, t_c	Observed values of $\frac{pv_0}{RT}$ and per cent. deviations from unity. $t = 0°$				Values of $\frac{pv_0}{RT}$ calculated from Berthelot's Equation and per cent deviations from observed values. $t = 0°$	
			$p = 0.1$ atmosphere		$p = 1$ atmosphere		$p = 1$ atmosphere	
				%		%		
He.....	4.00	−268°	1.000	**0.00**	1.0001	**0.01**	1.0006	**−0.05**
H_2.....	2.0155	−242	1.0002	**0.02**	1.0007	**0.07**	1.0005	**−0.02**
N_2.....	28.016	−146	0.9999	**0.01**	0.9995	**0.05**	0.9997	**+0.02**
O_2.....	32.0000	−119	1.0000	**0.00**	0.9992	**0.08**	0.9992	**0.00**
A.....	39.88	−117	0.9999	**0.01**	0.9992	**0.08**	0.9993	**0.01**
CH_4....	16.013	− 82	....	......	0.9979	**0.21**	0.9982	**0.03**
Kr.....	82.92	− 62	....	......	0.9978	**0.2**	0.9974	**0.04**
Xe.....	130.2	14.7	....	......	0.9931	**0.7**	0.9926	**0.05**
CO_2....	44.00	31	0.9993	**0.07**	0.9932	**0.68**	0.9931	**0.01**
N_2O....	44.016	36	0.9998	**0.02**	0.9931	**0.69**	0.9925	**0.06**
HCl....	36.4678	52	0.9992	**0.08**	0.9926	**0.74**	0.9925	**0.01**
NH_3...	17.0333	132	1.0003	**0.03**	0.9865	**1.35**	0.9883	**0.18**
SO_2....	64.07	157	0.9973	**0.27**	0.9759	**2.41**	0.9813	**0.54**

Table III

Values of $\frac{pv_0}{RT}$ for various saturated vapors at the normal boiling points, t_B, of the liquids. Illustrating the deviations of saturated vapors from the perfect gas law and from Berthelot's equation of state. For a perfect gas $\frac{pv_0}{RT} = 1$.

Vapor	Mol. wt., M	Critical temperature, t_c	Boiling point, t_B	Observed value of $\frac{pv_0}{RT}$ at $t_B{}^0$ $p = 1$ atmosphere	Per cent. dev. from unity	Value of $\frac{pv_0}{RT}$ from Berthelot's equation	Per cent. diff. between calc. and obs. values
He........	4.00	−268	−268.5	0.92	**8**	....	....
N_2........	28.016	−146	−195.7	0.95	**5**	0.95	**0**
O_2........	32.000	−119	−182.9	0.97	**3**	0.970	**0**
SO_2.......	64.1	157	− 10.0	0.98	**2**	0.98	**0**
n-C_5H_{12}...	72.1	197	36.3	0.956	**5**	0.958	**0.0**
n-C_7H_{16}...	100.0	267	98.4	0.948	**5**	0.955	**0.7**
C_6H_5F.....	96.0	287	85.2	0.974	**3**	0.967	**0.7**
C_6H_6......	78.1	289	80.1	0.977	**2**	0.967	**1.0**
$SnCl_4$......	260.3	318.7	114.1	0.964	**4**	0.964	**0**
C_6H_5Cl....	112.5	359	132.0	0.948	**5**	0.966	**1.9**

10. The Equations of van der Waals and of Berthelot. (*a*) **The Equation of van der Waals.**—In order to take into account the attractive forces between the molecules of real gases as well as the volume which the molecules themselves actually fill and thus to obtain an equation of state which would hold more accurately than the perfect gas law, especially for gases at high pressures, van der Waals[a] reasoned as follows: Consider a sphere of volume, v_0, filled with *one mole* of a gas at the pressure, p, and the temperature, T. Consider the layer of molecules which at any moment are just about to strike the inner surface of the sphere. The force of their impacts and therefore the pressure exerted by them will be diminished owing to the attractive force exerted by all the other molecules of the gas behind them. This force of attraction, f, will be proportional to the number of molecules at the surface and also proportional to the number in the interior of the gas and each of these in turn will be proportional to the density of the gas, or inversely proportional to the volume of the sphere. The force of attraction will, therefore, be proportional to the square of the density or inversely proportional to the square of the volume, or in mathematical language

$$f = aD^2 = \frac{a}{v_0^2} \tag{30}$$

where a is the proportionality constant and f is expressed in pressure units. Between the actual pressure, p, exerted by the gas molecules and the "perfect gas pressure," p_p, that is, the pressure which would be exerted if the force of attraction between the molecules were absent, there will evidently exist the relation,

$$p_p = p + \frac{a}{v_0^2} \tag{31}$$

Again the actual volume, v_0, of the sphere is not the volume v_p which the molecules have to move freely about in, but is greater than this by an amount, b, a quantity which is a function[2] of the total volume occupied by the molecules themselves. We have therefore,

$$v_p = (v_0 - b) \tag{32}$$

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[a] Joannes Diderik van der Waals, Professor of Theoretical Physics at the University of Amsterdam.

Now on substituting this corrected pressure and volume in equation (26) derived above, we have

$$\left(p+\frac{a}{v_0^2}\right)(v_0-b)=RT \tag{33}$$

which is **van der Waals' equation of state for one mole of a gas,** a and b being constants characteristic of the gas in question.

Experiments show that the general behavior of gases as displayed graphically by Figs. 1 and 2 is very well expressed mathematically by the equation of van der Waals. But although the equation of van der Waals correctly describes the general behavior of gases (and likewise of liquids) throughout the whole range of pressures and temperatures, it fails to represent quantitatively the actual experimental data in many instances. Various modifications (over 100 in all) of the equation have been proposed from time to time by different physicists with the purpose of diminishing this objection. The only one of these which we shall consider here is that of Daniel Berthelot.[a]

(*b*) **Berthelot's Equation.**—The characteristic constants, a and b, of van der Waals' equation have been found to bear a definite relation to the critical constants of the gas, from which in fact they may be computed. With the aid of this empirical relation Berthelot modified the equation of van der Waals by substituting in place of a and b their values expressed in terms of the critical constants of the gas. The resulting equation after an algebraic rearrangement may be expressed as follows:

$$pv_0=RT\left[1+\frac{9}{128}\frac{p}{p_c}\frac{T_c}{T}\left(1-6\frac{T_c^2}{T^2}\right)\right] \tag{34}$$

or

$$pv=NRT\left[1+\frac{9}{128}\frac{p}{p_c}\frac{T_c}{T}\left(1-6\frac{T_c^2}{T^2}\right)\right] \tag{35}$$

where p_c, the critical pressure, is the pressure required to condense the gas at its critical temperature, T_c, and the other quantities have the significance previously given to them. The numerical constants are empirical ones. It is evident that this expression approaches the perfect gas law as p decreases or T increases.

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[a] Daniel Berthelot (1865–   ) Professor of Physics in the University of Paris.

The equation of Berthelot not only expresses the general behavior of all pure gases thus far investigated but it does so with a high degree of accuracy, even for comparatively high pressures in some instances. This is well illustrated by problems 4, 5, and 6, below and also by the data shown in Table II where the values of $\frac{pv_0}{RT}$ calculated by means of this equation agree within the experimental errors with the values found by direct measurement. Even in the case of saturated vapors the results of experiment can be fairly well represented by Berthelot's equation, as shown by the data in Table III.

In using the Berthelot equation of state it should be remembered that it is applicable only to a *pure* gas, that is, to a gas in which at all temperatures and pressures up to the critical temperature and pressure, there is only one species of molecule. Moreover, in deriving his equation Berthelot explicitly assumes that the gas is not at or near its critical temperature and pressure and the equation is, therefore, only applicable to cases where this condition is also fulfilled. In other words the equation must not be applied to mixtures of gases, or to partially associated or dissociated gases, or to gases in the neighborhood of the critical point. Berthelot's equation had found its most important application in the exact determination of molecular and atomic weights as will be further explained in a following section.

Problem 4.—The measured value of $\frac{pv_0}{RT}$ for hydrogen at 0° is 1.006 for $p = 10$ atmospheres and 1.032 for $p = 50$ atmospheres. Compute the values by means of Berthelot's equation of state and compare with the measured values. (See Table XII for data required.)

Problem 5.—Make similar calculations for hydrogen at 100°. The observed values are 1.005 for 10 atmos. and 1.025 for 50 atmos.

Problem 6.—Make similar calculations for hydrogen at $-104°$. The observed values are 1.007 at 10 atmos. and 1.039 at 50 atmos.

Problem 7.—Make a similar calculation for CO_2 at 0° and 50 atmos. The observed value is 0.098. Note that 0° and 50 atmospheres are close to the critical values for this gas and that Berthelot's equation cannot be employed under these conditions as the result of your calculation indicates.

11. The Boyle Point.—From the observed values of $\frac{pv_0}{RT}$ given in Table II it is evident that at 0° the deviation from unity is positive in the case of hydrogen and helium and negative in the case of all the other gases. At lower temperatures, however, the deviation becomes negative in the case of hydrogen also, while at higher temperatures the deviation in the case of the other gases changes from negative to positive. In other words, there is for each gas a certain temperature, called the **Boyle point,** at which the gas obeys the laws of Boyle and Avogadro exactly. Above this temperature the deviation from this law is positive while below this temperature it is negative.

Problem 8.—By means of Berthelot's equation of state show that the Boyle point, T_I, of a gas is connected with its critical temperature by the relation, $T_I = 2.44\ T_c$. Compute the Boyle point for H_2, I_2, N_2, CO_2, CH_4 and NH_3.

12. Molecular Weights and Densities of Gases. (*a*) Approximate Molecular Weights from Gas Densities.

—Since $N = \frac{m}{M}$ and by definition $D = \frac{m}{v}$, the perfect gas law may evidently be written,

$$M = \frac{mRT}{pv} = \frac{DRT}{p} \tag{36}$$

from which the molecular weight of a gas can be calculated if its density, D, is known at some temperature, T, and pressure, p. It is frequently customary to refer the densities of gases to that of some gas employed as a standard. Thus the **density referred to oxygen** for any gas signifies the ratio of its density, D, to that of oxygen, D_O, at the same temperature and pressure. By dividing equation (36) by the corresponding equation for oxygen $\left(i.e., 32 = \frac{D_O RT}{p}\right)$ we have

$$M = 32\frac{D}{D_O} \tag{37}$$

or in words, **the molecular weight of any gas is equal to 32 times its density referred to oxygen.** Similarly if we choose to employ air as the reference gas, the above equation would read

$$M = 28.97\frac{D}{D_A} \tag{38}$$

where D_A is the density of air at the same temperature and pressure and 28.97, the so-called "molecular weight" of air, is simply the value which experiment gives for the quantity, M, in equation (36) when experimental data for air are substituted on the right-hand side of this equation.

Since real gases do not obey the perfect gas law exactly, except in the limiting case of very low pressures, equation (37) will give accurate values for the molecular weight of a gas only if we employ for $\frac{D}{D_O}$ the value approached by this ratio as the pressure approaches zero. It is quite possible, as we shall see in the second part of this section, to determine this limiting value with a high degree of accuracy so that this equation can be and is employed for the accurate determination of molecular and atomic weights. In the case of most gases, however, it is sufficient to determine the molecular weight approximately by means of equation (36) or (37) for the exact molecular weight can then be obtained simply by multiplying the combining weight of the substance by the small whole number (or whole number ratio) which gives a product most nearly equal to the approximate molecular weight.

Problem 9.—Calculate the approximate density of oxygen under standard conditions, that is, at 0° C. and a pressure of one atmosphere. (Its actually measured density under standard conditions is 1.4292 grams per liter.) Under the same conditions nitrogen weighs 1.2514 grams per liter. What is its density referred to oxygen? From the above data calculate the approximate value of its molecular weight. The analysis by Guye and Drouginin of one of the oxides of nitrogen gave the composition 1 part of oxygen and 0.43781 part of nitrogen. What is the combining weight of nitrogen in this compound? From this result and the approximate value for the molecular weight obtained above calculate a more exact value for the molecular weight of nitrogen.

(*b*) **Exact Molecular Weights from Gas Densities.**[3]—If we apply the reasoning of the preceding paragraphs to Berthelot's equation instead of to the perfect gas law, it will be easily seen that we shall obtain, in place of equation (36), the more exact relation,

$$M = \frac{DRT}{p}\left(1 + \left\{\frac{9T_c(T^2 - 6T_c^2)}{128\,p_cT^3}\right\}p\right) \tag{39}$$

which for the sake of brevity may be written

$$M=\frac{DRT}{p}(1+Ap) \tag{40}$$

where A is written in place of the expression in the braces. From this relation the molecular weight of a gas can be very accurately calculated as will be understood from the solution of the following problems:

Problem 10.—From the data given in Table XII calculate exact values for the molecular weights of O_2, N_2, Ar, N_2O and CH_4, with the aid of Berthelot's equation of state.

Problem 11.—At 0° and 0.5 atmosphere the density of neon is 0.44986 and that of sulphur dioxide is 1.4807 grams per liter. From these values and the densities under standard conditions (Table XII) compute the exact atomic weights of neon and of sulphur, without making any use of the critical data in either instance.

Problem 11 shows that Berthelot's method can be employed to determine molecular weights accurately without the necessity of knowing the critical constants. Measurement of the density of the gas at two different pressures is all that is required. This method of making the calculation is usually known as the **method of limiting densities** and is in general more reliable than the **method of critical constants,** illustrated by problem 10, because accurate values for the critical constants are rather difficult to obtain.

If as above in our treatment of the perfect gas equation we choose to make use of **densities referred to oxygen** instead of **absolute densities,** we have only to apply the same reasoning, that is, we divide equation (40) by the corresponding equation for oxygen,

$$32=\frac{D_OR T}{p}\ (1+A_Op) \tag{41}$$

and thus obtain in place of equation (37) the more exact relation,

$$M=32\frac{D}{D_O}\ \frac{1+Ap}{1+A_Op} \tag{42}$$

which, since at moderate pressures Ap and A_Op are small in comparison with unity, may also be written

$$M=32\frac{D}{D_O}(1+(A-A_O\,)p)=32\frac{D}{D_O}(1-\alpha p) \tag{43}$$

Problem 12.—Under standard conditions N_2O is 1.38450 times as dense as oxygen. Calculate its molecular weight by the method of critical constants employing equation (43) and taking the necessary critical data from Table XII.

Problem 13.—Under standard conditions the density of argon referred to oxygen is 1.24482. At the same temperature but at a pressure of 0.5 atmosphere it is 1.24626. Calculate the molecular weight of argon by the method of limiting densities employing equation (43).

Problem 14.—At 0° and a pressure of 0.5 atmosphere the density of oxygen is 0.71485 gram per liter and at 1 atmosphere it is 1.4290 grams per liter. From these two data calculate the numerical value of the gas constant, R.

Berthelot's methods of calculating exact molecular weights from gas densities are of particular value in connection with the inert gases of the argon group for since these gases have no combining weights their molecular and atomic weights cannot be accurately obtained by the ordinary method. In Table IV below, atomic weights obtained from gas densities are compared with those obtained from the combining weights for four elements. The agreement is within the experimental errors in every instance.

TABLE IV.—COMPARISON OF ATOMIC WEIGHTS DETERMINED FROM GAS DENSITIES WITH THOSE DETERMINED FROM COMBINING WEIGHTS

$O = 16.000$

(Four elements for which the most accurate data of both kinds are available.) (The values given are averages.)

Element	H	C	N	Cl
From gas density........	1.00775	12.004	14.008	35.461
From combining weight...	1.00775	12.00	14.008	35.460

PROBLEMS

(Assume the perfect gas laws.)

Problem 15.—What is the volume of 100 grams of ether vapor ($C_4H_{10}O$) at 10° and 60 cm.? What is its absolute density and its density referred to oxygen under the same conditions?

Problem 16.—What would be the volume of a mixture of 1 gram of carbon dioxide and 4 grams of carbon monoxide at 17° and a total pressure of 0.1 atmosphere? What would be the partial pressure of each gas?

Problem 17.—A mixture of N_2 and Ar at 371° and a pressure of 671 mm. contains 25 per cent. of N_2 by weight. Calculate (1) the partial pressure of each gas, (2) the absolute density of the mixture at 371° and 671 mm., and (3) the number of *molecules* (not moles) of each gas in 1 cubic millimeter of the mixture.

Problem 18.—A balloon open at the bottom and filled with hydrogen occupies a volume of 2000 cubic meters. Calculate in tons its lifting capacity at sea level and 27°.

Problem 19.—A Bessemer converter is charged with 1000 kg's. of iron containing 3 per cent. of carbon. How many cubic meters of air (containing 25 per cent., by weight, of oxygen) at 27° and 1 atm. are needed for the combustion of all the carbon, assuming 1/3 to burn to CO_2 and 2/3 to CO? What will be the partial pressures of all of the gases evolved by the converter?

Problem 20.—10 grams of solid iodine, I_2, are placed in a flask of one liter capacity and the flask is then filled with nitrogen at 20° and 750 mm. and sealed. The flask is then heated to 300°, at which temperature all of the iodine is vaporized. What pressure will be developed? The density of solid iodine is 4.66 grams per cc.

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JOURNAL ARTICLES: (2) T. W. Richards, Jour. Amer. Chem. Soc., **36,** 617 (1914), and J. J. van Laar, Proc. Amsterdam Acad. Sci., **17,** 464 (1914). (3) Numerous papers in the Jour. Chim. Phys. in recent years. See also Grinnell Jones, Jour. Amer. Chem. Soc., **32,** 514 (1910).

CHAPTER III

THE LIQUID STATE OF AGGREGATION

1. Liquefaction of a Gas or Vapor.—Consider any pure substance in the gaseous state enclosed in a transparent cylinder provided with a movable piston (Fig. 3). Let the cylinder be surrounded by some suitable bath by means of which its temperature can be kept constant at some point which may be anywhere between the critical temperature and the melting point of the substance. Now let the pressure upon the gas be gradually increased by forcing down the piston. The volume of the gas will be observed to gradually decrease as the pressure rises and after the pressure has been increased to a certain value (depending upon the nature of the substance and the temperature), a second phase, the **liquid phase,** will begin to appear. This phase usually appears first in the form of a fine mist which gradually settles to the bottom of the cylinder where it collects to a mass of liquid which is seen to be separated from the gaseous phase remaining in the upper part of the cylinder by a sharp bounding surface (Fig. 4). As soon as the liquid phase has appeared in the system no further increase of pressure can be produced as long as any of the gaseous phase remains. Any attempt to increase the pressure, ever so slightly, will result in the complete condensation (liquefaction) of all of the gas (Fig. 5). This constant pressure, which always prevails in every system composed of a gas and a liquid in equilibrium with each other at a given temperature is called the **vapor pressure** or vapor tension of the liquid at that temperature and is a characteristic property of the liquid. When all the gas has been liquefied (Fig. 5) the pressure on the liquid can then be increased indefinitely. When the pressure on a liquid is increased, however, the corresponding decrease in volume is ordinarily very much smaller than is the case with a gas. In other words the **compressibility** of liquids is comparatively small.

If we were to carry out the reverse of the above process, starting with a liquid under high pressure and gradually decreasing the pressure, we should observe, after the pressure had reached a value equal to the vapor tension of the liquid, that some of the liquid would evaporate and the system would again become heterogeneous owing to the appearance of the gaseous phase.

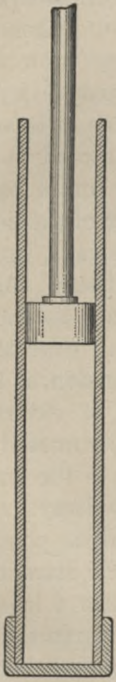

Fig. 3.

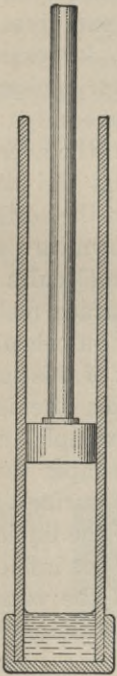

Fig. 4.

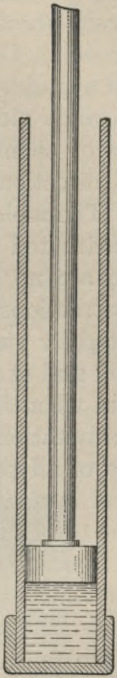

Fig. 5.

This behavior serves as a definite distinction between a liquid and a gas. (Cf. II, 1.)

2. General Characteristics of the Liquid State. Surface Tension.—The molecular condition in the interior of a body of liquid differs from that within the body of a gas in degree rather than in kind. The molecules of a liquid possess the same unordered or random motion characteristic of gas molecules and experiments show that in a given liquid the mean kinetic energy, $\frac{1}{2}mu^2$, of the moving molecules depends only upon the temperature, being independent of the mass of the molecules and the same for all molecules within a given liquid phase. The molecules of a liquid are, however, much closer together than those of a gas under low pressure and hence the mean free path (II, 1) of a liquid molecule is very short compared with that of a gaseous molecule. Moreover, the close proximity of the molecules to one another makes the effects of their mutual attractions very pronounced and gives rise to the phenomenon of surface tension. Consider, for example, any molecule within the body of a liquid. It is very powerfully attracted by the other molecules which closely surround it but since it is surrounded on all sides by them it is on the average attracted to a like degree in all directions so that the attractive forces balance one another.[1] The molecules in the surface layer of the liquid, however, are attracted only downward and sideways, not upward, since there are no liquid molecules above them. As a result of these attractions the surface molecules act as though they formed a tightly stretched but elastic "skin" over the surface of the liquid and as a result of this **surface tension,** as it is called, every liquid when freed from the influence of external forces (such as gravitation, for example) always assumes a spherical shape since of all possible shapes the sphere is the one having the smallest surface. The surface tension always acts so as to make the total surface of the liquid as small as possible.

A liquid in a vessel under the influence of the attraction of the earth assumes the shape of the vessel and has a level surface. This is because the earth's attraction largely overcomes the effect of the surface tension. At the point of contact between the surface of the liquid and the wall of the vessel, however, the surface is not level but always bends either upward or downward according to whether the liquid "wets" or does not "wet" the wall of the vessel. Thus water in glass always gives a *meniscus* which is concave upward while mercury which does

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[1] This attractive force is the same as that which is present in gases under high pressure and which was represented by the quantity, $\frac{a}{v^2}$, in van der Waals' equation (II, 10). In fact the equation of van der Waals will express very closely the variation of the volume of a liquid with changes in its pressure and temperature.

not wet glass gives a meniscus which is concave downward. This effect of surface tension which is seen at the boundary between the surface of the liquid and the enclosing wall is much more pronounced in the case of a liquid surface enclosed in a small tube or pore. If, for example, a capillary tube of glass is dipped into water, the water inside the capillary rises above the level of that outside (Fig. 6), while if such a tube is dipped into mercury, the level in the tube is depressed below the level outside. (Fig. 7.) In each case the result is a smaller *total* surface for the liquid. By total surface in this case is meant the surface of contact between the liquid and some other phase which it

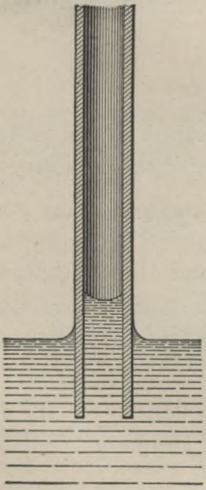

Fig. 6.

Fig. 7.

does not wet. The phenomenon of the rise (or depression) of liquids in capillaries or small pores of any description is known as **capillarity** and is due to the surface tension of the liquid. Many other familiar phenomena such as the behavior of soap-bubble films, and the absorption of water by a sponge, are the result of surface tension.

3. The Measurement of Surface Tension.—The unit of surface force, which is also called the **surface tension,** and is represented by the Greek letter gamma, γ, is defined as the force which acts upon a unit line, located within the surface. For example, if an attempt were made to increase the surface of a liquid by pulling upon an imaginary line 1 cm. long, located within the surface, the force tending to oppose the increase in surface is called the **surface tension,** γ, of the liquid. The magnitude of the surface tension is a characteristic property of the liquid. Of the various methods which are employed in its measurement we shall consider here only two of the most important ones.

(*a*) **The Capillary Tube Method.**—When a liquid rises (or sinks) in a capillary tube of radius, r, the height, h, to which it rises must evidently be such that the surface force, f_s, which is holding it up is just balanced by the force of gravity, f_g, which is pulling it down, that is,

$$f_s = f_g \tag{1}$$

Now the surface force is acting upon a line of length, l, which is equal to the inner circumference of the capillary tube and hence

$$f_s = l\gamma = 2\pi r\gamma \tag{2}$$

The force of gravity acting upon the volume, V, $(=\pi r^2h)$ of raised liquid is

$$f_g = mg = VDg = \pi r^2hDg \tag{3}$$

where m is the mass and D the density of the liquid and g is the acceleration due to gravity. Hence

$$f_s = f_g = 2\pi r\gamma = \pi r^2hDg \tag{4}$$

and the surface tension,

$$\gamma = \tfrac{1}{2}grhD \tag{5}$$

Problem 1.—The surface tension of water at 0° is 73.21 dynes per centimeter. How high will water at this temperature rise in a glass capillary 0.1 mm. in diameter?

(*b*) **The Drop-weight Method.**—When a drop of liquid forms slowly at a capillary tip (the tip of a pipette, for example), the size attained by the drop just before it breaks away from the tip will evidently depend upon the surface tension of the liquid.

Lohnstein[2] has shown that for a properly constructed tip the weight, w, of the drop which falls from it under the above conditions is given by the expression,

$$w = 2\pi r\gamma \mathrm{f}\left(\frac{r}{\sqrt{2\gamma/D}}\right) \tag{6}$$

where r is the internal radius of the tip and D is the density of the liquid. For a series of liquids it may be possible to choose a value for r such that the function, $\mathrm{f}\left(\frac{r}{\sqrt{2\gamma/D}}\right)$, will be practically constant for all the liquids in the series and under these circumstances the above expression becomes, approximately,

$$w = k\gamma \tag{7}$$

that is, the **drop-weights** of these liquids from this particular tip will be directly proportional to their surface tensions. Since drop-weights can usually be more easily and accurately measured than the capillary rise, the drop-weight method has been shown[3] by Morgan[a] to be especially valuable for determining the *relative* surface tensions of liquids. In order to determine the absolute value of the surface tension by the drop-weight method the capillary tip employed should be standardized by measurements with a liquid whose absolute surface tension is known. This standardization consists in determining the value of k in equation (7), or better still[4], in determining the values of r and of the function f ( ) in equation (6).

4. The Equations of Eötvös and of Ramsay and Shields.—The smallest surface which one molal weight of a liquid can have is its surface when in the form of a sphere. This surface, which is called the **molal surface,** and is represented by S_0, is evidently expressed by the relation,

$$S_0 \propto V_0^{\frac{2}{3}} = a\left(\frac{M}{D}\right)^{\frac{2}{3}} \tag{8}$$

where V_0 is the molal volume of the liquid, M its molal weight, and D its density. The product of the surface tension into

[a] J. Livingston R. Morgan (1872–). Professor of Physical Chemistry at Columbia University, New York City.

the molal surface, γS_0, evidently has the dimensions of work or energy and is called the **molal surface energy.** It represents the work involved in producing the surface, S_0, against the surface tension, γ. It is analogous to the molal volume energy, pv_0, in the case of a gas, (II, 4).

Between the molal surface energy of pure (*i.e.*, non-associated) liquids and the temperature there exists a relation, discovered by Eötvös[a] in 1886, which is perfectly analogous to equation (13, II) for gases. It is expressed mathematically by the equation,

$$\frac{-\mathrm{d}(\gamma S_0)}{\mathrm{d}\,t} = -\,a\,\frac{\mathrm{d}\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}}}{\mathrm{d}t} = const., \text{ or } \frac{-\,\mathrm{d}\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}}}{\mathrm{d}t} = K_s \qquad (9)$$

where K_s is a constant which has the same value for all pure liquids. Expressed in words this equation states that: **The temperature rate of change of the molal surface energy of a pure liquid is independent of the temperature and of the nature of the liquid.** The independence with respect to the temperature is illustrated by the data given in Table V.

Table V

Illustrating the equation of Eötvös, $\frac{-\,\mathrm{d}\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}}}{\mathrm{d}t} = K_s$. Values of K_s for benzene at various temperatures between 11° and 120°. $t_c = 288°$.

Measurements by Renard and Guye						Measurements by Ramsay						
$t° =$	11.4	31.2	55.1	68.5	78.3	80	90	100	110	120	200	250
$K_s =$	2.10	2.13	2.12	2.10	2.10	2.09	2.10	2.10	2.10	2.10	2.10	2.08

The integral of equation (9) is

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = -K_s t + K_s K' = K_s(K' - t) \qquad (10)$$

where $K_s K'$ is the integration constant. (Cf. equation 14, II.) Experiments made by Ramsay[b] and Shields using a number of

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[a] Baron Roland von Eötvös (*pr.* Āutvush), Professor of Physics in the University of Budapest.

[b] William Ramsay, K. C. B., F. R. S. (1852–). Professor of Chemistry (retired 1912) at University College, London.

different liquids showed that the constant, K', has approximately the value,

$$K' = t_c - 6 \tag{11}$$

where t_c is the critical temperature of the substance in each case. Equation (10), therefore, becomes

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = K_s(t_c - t - 6) \tag{12}$$

which is known as the Equation of Ramsay and Shields. As a rule, this relation does not hold unless $t_c - t$ is greater than 35°, that is, in the neighborhood of the critical temperature the relation fails. The constant, K_s, has the average value 2.1 ergs per degree, when γ is expressed in dynes. This value is based upon the assumption that the substance in the liquid state has the same molecular weight as it has in the gaseous state.

Equation (12) may also be written, $\gamma S_0 = k\theta$, where θ represents the temperature counted *downward* from a point 6° below the critical temperature of the liquid. This form of writing the equation brings out its resemblance to equation (16, II) for gases.

TABLE VI

Values of the constant, K_s, of the Eötvös equation, for a variety of substances calculated on the assumption that the molecular weight in the liquid state is the same as that in the gaseous state. $K_s = \frac{\mathrm{d}}{\mathrm{d}t}\left[-\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}}\right]$.

Data from Walden's Tabulation [Z. physik. Chem., **82**, 291 (1913)].

1. Elements and Inorganic Oxides and Halides

Substance	A	N_2	O_2	Cl_2	P_4	HCl	HBr	HI	CO	CO_2
Mol. wt.	39.9	28.0	32	71.92	124	36.46	80.97	128.0	28	44
$K_s =$	2.0	2.0	1.9	2.0	2.2	1.5(?)	2.0	2.0	2.0	2.2

Elements and Inorganic Oxides and Halides.—*Continued*

Substance	N_2O	SO_3	P_4O_6	$SOCl_2$	PCl_3	$SiCl_4$	CCl_4	$SnCl_4$	CS_2
Mol. wt.	34.02	80.06	220	120.0	137.4	170.1	153.8	260.8	76.14
$K_s =$	2.2	2.3	2.4	2.1	2.1	2.0	2.1	2.2	2.1

2. Hydrocarbons

Substance	C_6H_6	$C_6H_5CH_3$	n–C_6H_{14}	$C_6H_5C_2H_5$	m–C_8H_{10}
Mol. wt.	78.1	92.06	86.11	106.1	106.1
$K_s =$	2.1	2.0	2.1	2.1	2.2

Hydrocarbons.—*Continued*

Substance	$C_{10}H_8$	C_8H_{16}	n–C_8H_{18}	$(C_2H_5)_2$	$(C_2H_5)_2CH_2$	$C_{14}H_{14}$
Mol. wt........	128.1	102.1	114.1	58.08	71.1	182.1
$K_s =$	2.3	2.3	2.2	2.2	2.25	2.5

3. Esters and Ethers

Substance	HCO_2CH_3	$HCO_2C_3H_7$	$CH_3CO_2C_2H_5$	$C_2H_5CO_2CH_3$
Mol. wt.............	60.03	88.06	88.06	88.06
$K_s =$	2.0	2.1	2.2	2.2

Esters and Ethers.—*Continued*

Substance	$HCO_2C_5H_{11}$	$CCl_3CO_2C_5H_{11}$	$C_{12}H_{16}O_2$	$C_{20}H_{38}O_4$	$C_{57}H_{110}O_6$
Mol. wt.......	116.1	233.4	192.1	342.3	890.9
$K_s =$	2.1	2.46	2.6	3.3	5.7

4. Nitrogen Compounds

Substance	n–$C_3H_7NH_2$	$C_6H_5NH_2$	$C_6H_5N(CH_3)_2$	$C_6H_5NO_2$
Mol. wt..........	59.08	93.06	121.1	123
$K_s =$	1.5(?)	2.0	2.3	2.1

Nitrogen Compounds.—*Continued*

Substance	p–$C_6H_4OHNO_2$	$C_9H_{12}O_3N_2$	$C_{18}H_{15}Sb$	$C_{21}H_{21}N$
Mol. wt..........	139	196.1	351.3	287.2
$K_s =$	1.8	2.0	3.5	3.5

5. Hydroxyl Compounds

Substance	H_2O	CH_3OH	C_2H_5OH	HCO_2H
Mol. wt..........	18	32.03	46.1	46
$K_s =$	1.1	1.0	1.2	1.0

Hydroxyl Compounds.—*Continued*

Substance	n–C_3H_7OH	$C_3H_5(OH)_3$	C_6H_5OH	$C_{22}H_{42}O_2$
Mol. wt..........	60.1	92.06	94.1	354.3
$K_s =$	1.2	1.3	1.7	3.3

In Table VI are shown the values of this constant for a variety of different liquids. The data given in the first four sections of this table show that the value of this constant is close to 2.1 in the case of nearly all of the liquids given. These liquids are evidently of the most varied character and the temperatures are widely different in the different cases, ranging from −183° in the case of oxygen to 210° in the case of diphenyl methane,

$(C_6H_5)_2CH_2$. The last few liquids in each section of the table, however, have values of K_s which are considerably higher than 2.1 and it seems to be a fairly general rule that substances of very high molecular weight have values of K_s which are decidedly larger than 2.1. In fact Walden[a] and Swinne find[5] that this constant can be approximately calculated from the expression,

$$K_s = 1.90 + 0.011\ (\Sigma n \sqrt{A}) \tag{13}$$

where $\Sigma n \sqrt{A}$ is the sum of the square roots of the atomic weights of the elements in the compound, each square root being multiplied by the corresponding subscript as shown by the formula of the compound. Thus for tristearine, $C_{57}H_{110}O_6$, we have $\Sigma n \sqrt{A} = 57\ \sqrt{12} + 110\ \sqrt{1} + 6\ \sqrt{16} = 327$ and $K_s = 1.90 + 0.011 \times 327 = 5.5$ as against the observed value 5.7 given in the table.

For closely related substances the agreement of the K_s-values with one another is sometimes a very exact one, as shown by the figures given in Table VII, which are based upon relative surface tensions determined by the drop-weight method.

TABLE VII

Values of $K_s = \dfrac{\gamma_1 \left(\dfrac{M}{D_1}\right)^{\frac{2}{3}} - \gamma_2 \left(\dfrac{M}{D_2}\right)^{\frac{2}{3}}}{t_2 - t_1}$ by the drop-weight method for several organic liquids. K_s for benzene, C_6H_6, is taken as 2.120.

From measurements by Morgan and Higgins [Jour. Amer. Chem. Soc., **30**, 1065 (1908)].

Substance.........	C_6H_6	C_6H_5Cl	CCl_4	C_5H_5N	$C_6H_5NH_2$	C_9H_7N
$K_s =$	2.120	2.120	2.118	2.118	2.120	2.125

5. Molecular Weights of Liquids.—All of the K_s-values given in Tables V, VI, and VII, were calculated on the assumption that the molecular weight in the liquid is the same as that in the gaseous state in the case of every substance and the agreement between the K_s-values obtained with different liquids shows that for a great variety of substances and especially for related substances, equation (9) holds with considerable exactness. It should be noted, however, that just as good agreement would be obtained, if in each instance the molecular weight of the liquid

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[a] Paul Walden, (1863–). Professor of Inorganic and Physical Chemistry at the Polytechnic Institute, in Riga, Russia.

were assumed to be two or three or any other multiple of its molecular weight in the gaseous state. In other words, the agreement of the K_s-values obtained with different liquids does not necessarily show that they have the same molecular weight in the liquid and gaseous states. It does, however, indicate that if the molecular weight in the liquid state is not the same as in the gaseous state, then it must be some multiple of the latter which multiple is independent both of the nature of the liquid and of its temperature. It would be rather remarkable if such a condition were true for any other multiple than unity. Moreover we have additional evidence of quite another character that this multiple is, in fact, unity and that all substances which obey the Eötvös equation have the same molecular formulas in both the liquid and the gaseous states of aggregation. The Eötvös equation can, therefore, be employed for calculating the approximate value of the molecular weight of a **pure substance** in the liquid state from measurements of its surface tension at two temperatures. The calculation is most conveniently made from the relation,

$$\frac{\gamma_1\left(\frac{M}{D_1}\right)^{\frac{2}{3}}-\gamma_2\left(\frac{M}{D_2}\right)^{\frac{2}{3}}}{t_2-t_1}=K_s \qquad (14)$$

and the temperature difference, t_2-t_1, should be fairly large.

Returning now to section 5 of Table VI, it is evident that the liquids included in this section have K_s-values which are much smaller than those of the other liquids. Moreover, the K_s-values of these liquids are not constant with respect to variations in the temperature, that is, these liquids do not obey the equation of Eötvös. This is clearly shown by the K_s-values for water given in Table VIII. It is evident, therefore, that since

TABLE VIII

Showing the variation of the Eötvös constant, K_s, with the temperature in the case of water. Calculated on the basis of 18 for the molecular weight of water.

$$-K_s=\frac{\mathrm{d}}{\mathrm{d}t}\left[\gamma\left(\frac{18}{1}\right)^{\frac{2}{3}}\right]=0.685\,\frac{\mathrm{d}\gamma}{\mathrm{d}t}=0.685\,\frac{\Delta\gamma}{\Delta t_{10^\circ}}$$

Observer	Morgan and McAfee								Ramsay and Shields
t° =	5	15	25	35	45	55	65	75	140
K_s =	1.08	1.11	1.14	1.16	1.20	1.23	1.26	1.30	*ca.* 1.6

the Eötvös equation is not obeyed by these liquids it cannot be logically employed in calculating their molecular weights.[6] If it is so employed, the molecular weights thus calculated are found to vary with the temperature and to be from two to three times as large as the molecular weights in the gaseous state. The most probable explanation of the behavior of these liquids is that they are not pure substances in the sense in which we have defined the term (I, 2), that is, they do not consist of a single species of molecule but of a mixture of two or more species in equilibrium with one another. Indeed there is abundant evidence from other sources that liquid water is a mixture of the following species of molecules, H_2O, $(H_2O)_2$, $(H_2O)_3$ and perhaps higher polymers, all in chemical equilibrium with one another. Equilibrium mixtures, of this character which in many respects behave like pure substances are usually called **associated substances,** to distinguish them from **pure substances** in the true sense of the term which are non-associated and contain but one species of molecule. Substances of the latter class in the liquid state are also sometimes called "**normal liquids**" for the same reason.

Problem 2.—From a certain capillary tip the drop-weight of benzene at 11.4° is 35.239 milligrams and at 68.5° it is 26.530 milligrams. Its densities at the same temperatures are 0.888 and 0.827 grams per cubic centimeter respectively. Calculate the critical temperature of benzene.

Problem 3.—From the same tip as in problem (2) the drop-weight of chlorbenzene is 41.082 milligrams at 8.2° ($D = 1.120$) and 32.054 milligrams at 72.2° ($D = 1.0498$). Calculate its molecular weight in the liquid state. Calculate also its critical temperature [t_c observed = 360°].

Problem 4.—From the same tip the drop-weight of aniline, $C_6H_5NH_2$, at 51.7° is 45.903 milligrams ($D = 0.9944$). Calculate the critical temperature of aniline [t_c observed = 426°].

6. Viscosity and Fluidity.—The internal friction or the resistance experienced by the molecules in moving around in the interior of a body is termed its viscosity. The viscosity of gases is very low, that of solids very high, while that of liquids includes a wide range of variation. Some liquids, like ether, are very *mobile,* while others such as pitch and tar are very *viscous.* The unit of viscosity, called the **coefficient of viscosity** or simply the **viscosity,** is represented by the Greek letter eta, η, and is defined as the force required to move a layer of the substance of unit area, through a distance of unit length, in unit time, past an adjacent stationary layer a unit distance away. The viscosity of fluids is commonly measured by determining the time of flow of a measured volume of the fluid through a standardized capillary tube, under a definite difference of pressure. The more viscous a liquid, the more slowly it flows.

The reciprocal of viscosity is called **fluidity,** $\phi, \left(\phi = \frac{1}{\eta}\right)$ and is sometimes a more convenient quantity to employ than the viscosity itself. The fluidity is evidently a measure of the tendency of substances to flow while its reciprocal, the viscosity, is a measure of the resistance to flow. The property of flowing with considerable ease is possessed by all gases and by most liquids and they are commonly classed as **fluids** for this reason.

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CHAPTER IV

LIQUID-GAS SYSTEMS

1. The Molecular Kinetics of Vaporization.—The molecules of a liquid are in a state of constant unordered motion like those of a gas but they collide with one another much more frequently owing to the greater number of them in a given volume. These collisions take place without loss of energy and although the velocities of the different molecules vary all the way from zero to very large values there is a certain mean velocity corresponding to the mean kinetic energy ($\frac{1}{2}mu^2$) which for a given liquid depends only upon the temperature. This mean velocity is too small to allow the molecules possessing it to escape from a free surface of the liquid. There are always present, however, some molecules possessing a much higher velocity than this mean velocity, so that if the liquid is brought into contact with a vacuous space, some of these rapidly moving molecules will escape through the surface of the liquid into the space above it. In other words, some of the liquid will evaporate. This evaporation will continue until the vapor above the liquid reaches a certain definite pressure, determined only by the temperature and by the nature of the liquid. This pressure is the **vapor pressure** or vapor tension of the liquid. It is evidently that pressure at which the rate of escape into the gas phase of the more rapidly moving liquid molecules is exactly balanced by the return into the liquid phase of the more slowly moving gaseous molecules. Thus while a vapor which is not in contact with its liquid may have any pressure from zero up to a value somewhat exceeding the vapor pressure, a vapor in contact with its liquid can have only one pressure at a given temperature, namely, the **vapor pressure** of the liquid at the temperature.

If a liquid is brought in contact with a space containing some other gas at a moderate pressure (say not exceeding one atmosphere), then if this other gas is nearly insoluble in the liquid, it follows from Dalton's law of partial pressures (II, 6) that approximately the same amount of liquid will evaporate into the space as would if the second gas were not present. Thus the vapor tension of water in contact with air is approximately the same as its vapor pressure in a space containing no second gas. If the pressure of the second gas is large or if it is appreciably soluble in the liquid, this principle is no longer valid. In other words, it is strictly valid only for the limiting case of an insoluble gas at a very small pressure and in any actual case it holds more exactly the more nearly these two conditions are fulfilled.

In Table IX the vapor pressures of a number of liquids at 20° are given.

TABLE IX.—VAPOR PRESSURES OF VARIOUS LIQUIDS AT ROOM TEMPERATURE (20°)

Liquid	Formula	Vapor pressure, mm. Hg	Liquid	Formula	Vapor pressure mm. Hg
Mercury........	Hg	0.0016	Ethyl chloride......	C_2H_5Cl	996.2
Di-amyl........	$C_{10}H_{22}$	2.7	Sulphur dioxide . . .	SO_2	2,500
Water..........	H_2O	17.54	Chlorine...........	Cl_2	5,040
Ethyl alcohol...	C_2H_5OH	44.0	Ammonia..........	NH_3	6,800
Benzene........	C_6H_6	74.7	Hydrogen sulphide .	H_2S	14,100
Methyl acetate..	CH_3COOCH_3	169.8	Carbon dioxide.....	CO_2	42,500
Ethyl ether.....	$(C_2H_5)_2O$	442.0			

2. Heat of Vaporization.—Since only those molecules can escape from the liquid phase which possess kinetic energies considerably greater than the mean kinetic energy, it is clear that the mean kinetic energy of the remaining molecules must have a lower value after the escape of the more rapidly moving ones. In other words the temperature of the liquid tends to fall during evaporation and in order to maintain it at a constant value, heat must be added to the liquid from some external source. This heat is called the latent heat of vaporization. The **molal heat of vaporization,** L_v, of a liquid under constant pressure, P, at any temperature, T, is the quantity of heat which it is necessary to add to the liquid in order to maintain its temperature at T while one gram molecular weight of the liquid evaporates. The heat of vaporization varies with the nature of the liquid, with its temperature, and (to a very slight extent) with the pressure upon it.

3. Boiling Point.—When a liquid is heated under a definite external pressure (water under the pressure of the atmosphere, for example), its vapor pressure increases with rise in temperature until finally a temperature is reached at which bubbles of vapor form and rise from within the body of the liquid and escape into the space above it. The liquid is then said to boil. The **boiling point** is defined as the temperature at which a liquid is in equilibrium with its vapor, when the vapor pressure is equal to the total pressure upon the liquid. The temperature indicated by a thermometer placed in a boiling liquid is usually not its boiling point, for unless special precautions are taken a liquid does not boil under equilibrium conditions. In order to secure equilibrium and to measure the temperature corresponding to it, it is necessary to bring an intimate mixture of vapor and liquid both under the same total pressure, into contact with the thermometer under certain conditions, the details of which belong to the subject of methods of physical measurements, which it is not the purpose of this book to deal with.

Since the vapor pressure of a liquid always increases with increase of temperature, it follows from the definition of boiling point that it also must increase with the external pressure upon the liquid. The boiling point of a liquid under a pressure of one atmosphere (76 cm. of Hg) is called the **normal boiling point** and, unless otherwise specified, it is this temperature which is meant when the term boiling point is used.

4. The Rule of Ramsay and Young.—If T_{A} and T_{B} are the absolute boiling points of two related, pure (non-associated) substances at the pressure, p; and T'_{A} and T'_{B} their boiling points at some other pressure, p', Ramsay and Young[a] found that these temperatures were connected by the following relation, applicable from the lowest pressures up to the critical point,

$$\frac{T'_{\mathrm{A}}}{T'_{\mathrm{B}}}=\frac{T_{\mathrm{A}}}{T_{\mathrm{B}}}+c(T'_{\mathrm{A}}-T_{\mathrm{A}}) \qquad (1)$$

where c is a constant which is smaller the more closely related the substances are, being practically zero for very closely related substances, such as brombenzene, C_6H_5Br, and chlor-

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[a] Sydney Young (1857–). Professor of Chemistry in the University of Dublin.

benzene, C_6H_5Cl, for example. Table X shows the values of $\frac{T_B}{T'_B}$ for a series of esters. The above rule evidently requires that this ratio should be constant, if $c = 0$. It evidently varies but slightly for these closely related substances.

TABLE X

Illustrating the Rule of Ramsay and Young regarding the boiling points of closely related substances

Substance	T_B 760 mm.	T'_B 200 mm.	$\frac{T_B}{T'_B}$
Methylformate	305.3°	273.7°	1.115
Methylacetate	330.5	296.5	1.115
Methylpropionate	352.9	316.7	1.114
Methylbutyrate	375.3	336.9	1.114
Methylvalerate	389.7	350.2	1.113
Ethylformate	327.4	293.1	1.117
Ethylacetate	350.1	314.4	1.114
Ethylpropionate	371.3	333.7	1.113
Ethylbutyrate	392.9	352.2	1.116
Ethylvalerate	407.3	365.3	1.115
Propylformate	354.0	318.0	1.113
Propylacetate	373.8	336.1	1.112
Propylpropionate	395.2	355.0	1.113
Propylbutyrate	415.7	374.2	1.111
Propylvalerate	428.9	385.6	1.112

5. Correction of Boiling Points to Normal Pressure. The Rule of Crafts.—In practice the boiling point of a liquid is usually determined at the atmospheric pressure prevailing at the time the measurement is made. For purposes of record and of comparison, it is desirable to know the normal boiling point. The necessary correction which must be applied in order to reduce the observed boiling point to the normal pressure can be conveniently calculated by means of a rule, proposed by Crafts[a] which is based upon that of Ramsay and Young. The correction, Δt, to be *added* to a boiling point, T_B, on the absolute scale, determined at a pressure of P mm, in order to reduce it to 760 mm is given by the relation,

$$\Delta t = cT_{B_0}\,(760 - P) \qquad (2)$$

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[a] James Mason Crafts (1839–). Professor (retired 1900) of Organic Chemistry at the Massachusetts Institute of Technology.

where the constant, $c = \frac{1}{T_{B_0}} \frac{\mathrm{d}T_B}{\mathrm{d}P}$, T_{B_0} being the normal boiling point of the liquid. The value of c for pure (non-associated) liquids is about 0.00012 but it varies somewhat with the nature of the liquid and in practice the value for some liquid which is related as closely as possible to the one under examination should be employed in calculating the correction. Table XI gives the values of $c \times 10^4$ for a variety of different liquids. The constant c varies somewhat with P and the rule of Crafts is, therefore, accurate only when $760 - P$ is small.

TABLE XI

Values of the constant, $c \left(= \frac{1}{T_{B_0}} \frac{\mathrm{d}T_B}{\mathrm{d}P}\right)$ in the Crafts' equation, $\Delta t = cT_{B_0}(760 - P)$, for the correction of boiling points to normal pressure.

Substance	$c \times 10^4$	Substance	$c \times 10^4$
Mercury	1.20	Caprylic acid	1.01
Sulphur	1.27	Phenol	1.0
Tin	1.3	Ethyl ether	1.29
Oxygen	1.43	Acetone	1.19
Argon	1.35	Propyl acetate	1.14
Chlorine	1.35	Methyl formate	1.19
Hydrochloric acid	1.3	n-Hexane	1.23
Ammonia	1.35	n-Octane	1.20
Carbon dioxide	0.8	Benzene	1.22
Carbon monoxide	1.6	p-Xylene	1.36
Sulphur dioxide	1.0	Diphenyl methane	1.25
Carbon disulphide	1.1	Dimethyl aniline	1.15
Carbon tetrachloride	1.6	o-Nitrotoluene	0.98
Stannic chloride	1.35	Anthraquinone	1.15
Boron trichloride	1.3	Benzophenone	1.10
Water	1.01	Benzoyl chloride	1.17
Ethyl alcohol	0.97	Camphor	1.16
Propyl alcohol	0.97	Menthon	1.15
n-Butyl alcohol	0.90	Naphthalene	1.19
Acetic acid	1.0	Phthalic anhydride	1.19
Propionic acid	1.0	Sulphobenzide	1.04

Problem 1.—The following boiling points have been determined at the pressures indicated: di-isopropyl, 60° at 807 mm; methyl chloride, −20° at 1.16 atmos.; methyl alcohol, 60° at 625.0 mm; germanium tetrachloride, 70.7° at 0.67 atmos.; heptylic acid, 218.1° at 700 mm; camphor, 206.7° at 731 mm; p-cresol, 198.5° at 700 mm; hydrogen sulphide, −60° at 770 mm; zinc, 933° at 767 mm; bromine, 56.3° at 700 mm; argon, −186.2° at 757.3 mm. Calculate the normal boiling point.

6. Trouton's Rule.[2]—This rule states that for closely related substances the molal heat of vaporization at the normal boiling point, divided by the normal boiling point on the absolute scale is a constant, that is,

$$\frac{L_v}{T_{B_0}} = const. = 22 \tag{3}$$

A modified Trouton's[a] rule proposed by Nernst[b] is the following,

$$\frac{L_v}{T_{B_0}} = 9.5 \log_{10} T_{B_0} - 0.007\ T_{B_0} \tag{4}$$

which is more accurate and includes a larger variety of substances.

Problem 2.—Calculate the heats of vaporization of six of the substances given in Table XII. Look up the experimentally determined values for the same substances and compare. Use the Landolt-Bornstein Physikalisch-Chemische Tabellen (4th ed., 1912) and the "Annual Tables of Physical and Chemical Constants" in looking for the experimental values.

7. The Critical Phenomena.—The significance of the terms critical temperature and critical pressure has already been briefly explained at the point where they were first employed in our treatment of the properties of gases. We shall now take up in considerable detail the phenomena which one observes when a pure liquid is gradually heated in a closed vessel in contact with its vapor. For this purpose we will imagine our liquid enclosed in a transparent cylinder provided with a movable piston. To take a concrete case suppose we start with liquid isopentane, a substance which has been very fully investigated by Young. Starting with 1 gram of the liquid under an initial pressure of about 42 meters of mercury (Fig. 5) and at a temperature of 160°, we will gradually decrease the pressure, keeping the temperature constant, and in order to see clearly the relation between the volume of the isopentane and the pressure upon it we will construct a diagram in which the pressures will be plotted as ordinates and the corresponding volumes as abscissæ. Such a diagram is shown in Fig. 8, the small circles representing observed values. Starting at the point, A, therefore, ($p = 25.2$, $v = 2.4$) we gradually

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[a] Frederick Thomas Trouton, F. R. S., Professor of Physics in the University of London.

[b] Walther Nernst (1864–). Professor of Physical Chemistry and Director of the Physico-Chemical Institute at the University of Berlin.

decrease the pressure which follows the line, AB. When the point, B, is reached where the pressure is 16.3 meters of mercury the vapor phase appears, since 16.3 is the vapor pressure of isopentane at 160°. The abscissa of this point, 2.38 cc, is evidently

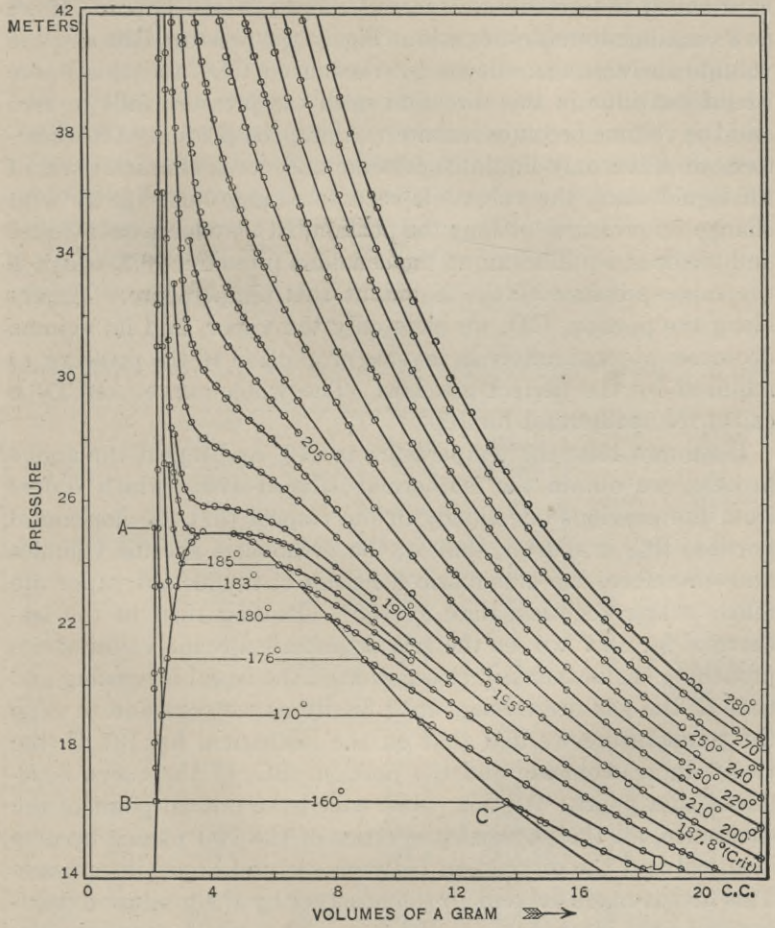

FIG. 8.—Isotherms of Isopentane.

the specific volume of liquid isopentane at 160° *when under its own vapor pressure.* It is called the **orthobaric** specific volume of the liquid. As we continue to raise the piston the liquid continues to evaporate (Fig. 4) and the total volume consequently increases along the line, BC, while the pressure remains perfectly constant. When the point, C, is reached all of the liquid has evaporated and the abscissa of this point, 13.72 cc, is therefore the specific volume of the saturated vapor at this temperature. It is called the orthobaric specific volume of the vapor. If we now continue to raise the piston (Fig. 3) the pressure falls and the volume increases as shown by the curve CD, and this curve would continue in this direction until the pressure falls to zero and the volume becomes infinite. Along the portion, AB, therefore, we have only liquid isopentane and, as is characteristic of the liquid state, the volume is seen to change but slightly with change in pressure. Along the portion, BC, we have both liquid and vapor in equilibrium at the constant pressure, 16.3, which is the vapor pressure of the liquid at this temperature. Finally along the portion, CD, we have only the vapor, and its volume decreases approximately in inverse proportion to the pressure, as required by the perfect gas law. The whole curve, ABCD, is called the **isothermal** for 160°.

If we now raise the temperature to 170° and repeat the above process, we obtain the isothermal labeled 170°, which differs from the previous one chiefly in the respect that the horizontal portion, BC, is shorter, that is, the orthobaric specific volumes and, therefore, the orthobaric densities of liquid and vapor are much nearer together than at 160°. Passing then to the isothermal for 180° we see the two orthobaric specific volumes approaching each other still closer, that of the liquid increasing and that of the gas decreasing, until finally as we continue to raise the temperature we find that on the isothermal for 187.8°, the two volumes coincide and the portion, BC, of the curve is reduced to a point. At this point, called the **critical point** of the substance, all the physical properties of the two phases become identical and the distinction between gas and liquid disappears. This fact is made evident to the observer by the gradual flattening and final disappearance of the meniscus which separates the two phases, showing that with rising temperature the surface tension of the liquid gradually decreases and finally becomes zero at the critical point. The temperature of the critical isotherm is called the **critical temperature,** t_c, of the substance. The corresponding pressure, which is evidently the vapor pressure of the liquid at the critical temperature as well as the maximum vapor pressure which the liquid can have, since it ceases to exist at this point, is called the **critical pressure,** p_c, of the substance. The density of the substance at the critical point is called the **critical density,** D_c, and the reciprocal of the density or the specific volume is called the **critical volume,** v_c. The critical constants of a number of substances are given in Table XII. Above its critical temperature no gas can be caused to liquefy no matter how great a pressure is put upon it. In Fig. 8 the isothermals above the critical point show at first a flattening in the neighborhood of the critical volume. With increasing temperature, however, this flattening gradually disappears and the isothermals smooth out into the hyperbolas of a perfect gas, hyperbolas which, in other words, are graphs of the equation,

$$pv = const.$$

TABLE XII.—PHYSICAL PROPERTIES OF SOME OF THE PRINCIPAL GASES AND VAPORS

Gas	Density under standard conditions D g. per liter	Melting point, T_F	Boiling point, T_{B_0}, 760 mm.	Critical temperature, T_c	Critical pressure, p_c atmospheres	Critical density, D_c grams per cc
He	0.1785	<3°	4.25°	5.25°	2.26	0.07
H_2	0.08987	14.1	20.3	31[2]	13.4[2]	0.033
Ne	0.9002	30	53	55	29.	....
N_2	1.2507	62.5	77.3	125.96	33.490	0.311
A	1.7809	85.1	87.2	150.7	48.0	0.509
O_2	1.4290	46	90.1	154.25	49.713	0.4292
NO	1.3402	112.5	122.5	179.5	71.2	....
CH_4	0.7168	89	108.3	191.2	54.9	....
Kr	3.708	104	121.3	210.5	54.3	....
Xe	5.851	133	163	289.0	58.0	1.15
CO_2	1.9768	216.3	194.7	304.1	72.9	0.448
N_2O	1.9777	170.3	183.2	309.5	71.65	....
HCl	1.6394	161.6	189.9	324.5	81.6	0.41
NH_3	0.7708	194.8	239.5	406.0	112.3	....
Cl_2	3.1674[1]	171.0	239.4	417.0	79.6	....
SO_2	2.9266	200.7	263	430.3	77.7	0.513
n-C_5H_{12}	liquid	125.6	309.3	470.3	33.026	0.2323
n-C_7H_{16}	liquid	176.0	371.5	540.0	26.881	0.2341
C_6H_5F	liquid	232.0	358.3	559.7	44.619	0.3541
C_6H_6	liquid	278.5	353.4	561.7	47.89	0.3045
$SnCl_4$	liquid	240	387.2	591.8	36.95	0.7419
C_6H_5Cl	liquid	228	405.1	632.3	44.631	0.3654
H_2O	liquid	273.1	373.1	647.0	217.5	0.4
Hg	liquid	235.2	630.1	>1550.0	....	....

[1] Jaquerod and Tourpaian [J. Chim. Phys., **11,** 274 (1913)] give 3.214.

[2] Bulle [Physik. Z., **14,** 860 (1913)] gives 32° and 11.0 atmos.

Problem 3.—What is the value of the latent heat of vaporization of a liquid just below its critical temperature?

Problem 4.—Describe a process by which it is possible to start with liquid water at 10° under a pressure of one atmosphere and convert it completely into steam at 110°, without causing it to "evaporate," that is, without at any time having two phases in the system.

8. The Rule of Cailletet[a] and Mathias.[b]—This rule states that the mean of the two orthobaric densities of a pure (non-associated) substance is a linear function of the temperature, or mathematically,

$$\frac{D_l+D_g}{2}=a+bT \qquad (5)$$

This is illustrated graphically in Fig. 9 which is self explanatory.

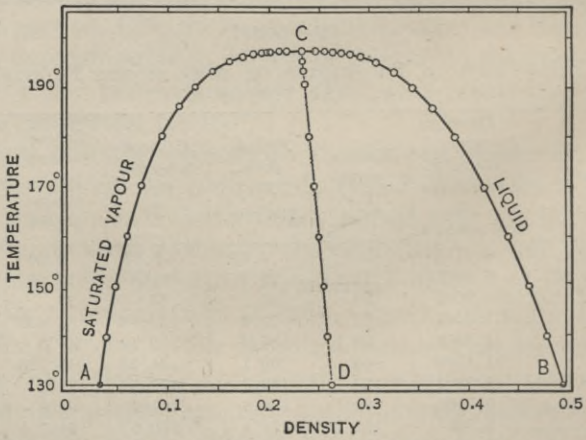

FIG. 9.—Illustrating the Rule of Cailletet and Mathias. The points along CD represent the means of the two corresponding orthobaric densities.

One of the principal uses of this rule is in determining the value of the critical density of a substance, as it is usually not possible to measure this density directly. The method of applying the rule to such cases is illustrated by problem 5. As a rule the relation holds more exactly in the immediate neighborhood of the critical point than it does at lower temperatures.

[a] Louis Cailletet, Iron Master at Chatillon-sur-Seine.

[b] E. Mathias, Professor of Physics and Meteorology at the University of Clermont, France.

Problem 5.—The critical temperature of normal pentane is 197.2°. At 150° the orthobaric densities of this substance are 0.4604 and 0.0476 respectively. At 190° they are 0.3445 and 0.1269. Calculate the critical density of normal pentane. [Observed value, 0.2323.]

9. Superheating and Supercooling.—When a body of liquid is gradually heated from the outside it is frequently possible to raise its temperature considerably above its boiling point—as much as 200° in the case of water. Such a liquid is said to be **superheated.** When a liquid is heated in a vessel by the application of heat to the bottom of the vessel, the lower layers of the liquid become superheated and from time to time portions of these superheated layers change into vapor with explosive violence causing the phenomenon known as "*bumping.*" Superheating and hence bumping can be prevented or greatly reduced by having some of the vapor phase in contact with the liquid at the point where heat is applied. In practice this is usually attained by introducing pieces of capillary tubing or of porous porcelain plate. The small capillaries become filled with vapor and the presence of the vapor tends to prevent superheating of the liquid which thus boils quietly, the bubbles of vapor forming and rising from the point of contact of the liquid with the vapor held in the capillaries.

The reverse of superheating, that is **supercooling,** is frequently observed when a gas or vapor is cooled. It may be cooled considerably below the temperature at which its pressure becomes equal to the vapor pressure of the liquid, without the appearance of any liquid phase in the system. If a single drop of liquid be introduced, however, condensation immediately occurs. In fact as a general rule when any phase, whether liquid, gas, or solid, reaches a condition where it ought normally to change over into another state of aggregation or another phase, this change frequently does not take place at once but supercooling or superheating occurs instead. The introduction of a trace of the second phase, however, is usually sufficient to bring about the change and to prevent any great degree of supercooling or superheating. Mechanical agitation or the presence of small particles, such as dust, frequently has a similar effect.[3]

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CHAPTER V

THE CRYSTALLINE STATE OF AGGREGATION

1. General Characteristics of the Crystalline State.—When a substance in the gaseous state at any temperature below its melting point is subjected to gradually increasing pressures, or when a substance in the liquid state is gradually cooled, a point will usually be reached where a third state of aggregation, the crystalline state, appears in the system. This state of aggregation is characterized by a very slight compressibility, usually much smaller even than that of the liquid state. Examination of any substance in the crystalline state shows that it is made up of an aggregation of individuals having a definite geometric form, which form is one of the characteristic properties of the substance. These geometric forms are called crystals and the physical properties of these crystals bear a close connection to the crystalline form. A crystal may, in fact, be defined as a homogeneous body possessing definite and characteristic vector properties, that is, properties which are different in different directions through the crystal. Such a body is called an **anisotropic** body (I, 8). Thus, for example, the conductivity for heat or for electricity measured in one direction through a crystal may be different from that measured in a direction at right angles to the first, and the index of refraction for light usually depends upon the direction in which the light is sent through the crystal. The systematic description and classification of the different geometric forms displayed by crystals and the relation of these forms to the physical properties of the crystals belongs to the subject of crystallography, which will not be entered upon in this book.

In the case of most crystalline substances the crystals possess **rigidity,** that is, they offer a resistance to deformation by mechanical force. For this reason they are called **solid** substances and because the property of solidity is common to the large majority of crystalline substances, the crystalline state is commonly spoken of as the **solid state.** The property of solidity is by no means restricted to crystals, however, but is possessed to a very pronounced degree by some liquids. Moreover, there are some crystals which possess scarcely any appreciable solidity. The term crystalline state is, therefore, a better name for this state of aggregation than the more customary one of "solid state."

When a crystalline substance is gradually heated under constant pressure (that of the atmosphere, for example) it either completely evaporates, thus changing into a gas or vapor, or else, if the pressure upon it be sufficiently great, it loses its crystalline form and changes into the liquid state, as soon as a definite temperature is reached. This temperature, which depends to a slight extent upon the pressure, is called the melting point of the substance and is one of its most characteristic properties. The molecular kinetics of the melting process and the probable molecular condition within a crystal will be considered in the next chapter.

2. Liquid Crystals.—Most crystals are rigid and will fracture when subjected to pressure, but many substances are known to form crystals in which the crystal forces are so weak that the crystals can be easily distorted and will even flow, form drops and rise in capillary tubes under the influence of the surface tension forces. They are called **liquid crystals**[1, 2] or crystalline liquids. In common with solid crystals, however, they possess a definite melting point and the optical properties characteristic of the crystalline state. The property of flowing under pressure is not confined to substances usually called liquid crystals, however, but is probably possessed to some extent by all crystals. Thus ice, which will fracture if struck, will gradually flow, if subjected to great pressure. This gradual flow is probably at least partially responsible for the movement of glaciers down mountain sides and through valleys.

3. Polymorphism and Transition Point.—When a crystalline substance is gradually heated we find in some cases that when a certain temperature is reached a change occurs in which this crystal form disappears and a second crystal form appears. That is, the substance has the property of existing in more than one form of crystals. This property is known as **polymorphism.** The transition of one form into the other is usually attended by a pronounced volume change and an appreciable evolution or absorption of heat. The two forms of crystals are perfectly distinct and must be regarded as *different crystalline phases.* At a certain temperature, called the **transition or inversion temperature,** these two phases can exist in equilibrium with each other. Above this temperature one form only is stable and below this temperature the other form only is stable. The quantity of heat absorbed when one mole of a substance in the crystalline form, A, changes to the form, B, at the transition temperature is called the **molal heat of transition** from the form, A, to the form, B, at this temperature. The transition temperature varies slightly with the pressure.

The nature of the molecular kinetics of the process of transition may be inferred from that of the process of fusion which will be described in the next chapter. Owing to the restricted character of the molecular motion in a crystal (see VII, 1), the process of transition from one form to the other is frequently a very slow one and if the transition temperature happens to be rather high, both forms can be kept for practically an indefinite period at ordinary temperatures although only one of these forms is strictly stable under these conditions. The unstable form has still the *tendency* to change over to the other even though no change can be observed over long periods of time. (Cf. Supercooling of Liquids, VII, 3.) Thus two crystalline modifications of calcium carbonate, calcite and aragonite, are found in nature although only the former is "stable" at ordinary temperatures.

4. Isomorphism and the Rule of Mitscherlich.—It frequently happens that two substances of analogous composition such as arsenic acid, H_3AsO_4, and phosphoric acid, H_3PO_4, form crystals which resemble each other very closely, so closely in fact that when a crystal of one is placed in a solution of the other the second will crystallize out upon the first and from a solution containing both substances mixed crystals, that is, homogeneous crystals containing both substances, can be obtained. Such substances are said to be **isomorphous.** On the basis of this behavior Mitscherlich[a] proposed a rule which was once of con-

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[a] Eilhardt Mitscherlich (1794–1863). The son of a preacher. He devoted himself first to the study of history, philology and oriental languages. In 1821 he became Professor of Chemistry in the University of Berlin.

siderable importance in deciding which multiple of the combining weight of an element was its atomic weight. This rule may be stated as follows: Two isomorphous substances have analogous molecular formulas. Thus, in the case cited above, if the formula of phosphoric acid were known to be H_3PO_4, then we could infer that that of arsenic acid was H_3AsO_4 and not $H_3As_2O_4$ or H_6AsO_8, for example, and, therefore, if the per cent. of arsenic in the compound were determined, its atomic weight could be calculated. The rule of Mitscherlich was used quite extensively by Berzelius[a] for fixing atomic weights but is seldom employed to-day as it is not a very safe one, several very marked exceptions to it being known,[3] and also because we now have much more satisfactory methods which can be used for the same purpose.

5. Relations between Crystal Form and Chemical Constitution.—Mitscherlich's rule of isomorphism was one of the earliest attempts to correlate crystal form with chemical constitution. In recent years the subject has again received considerable attention and a theory has been formulated by means of which many of the forms displayed by crystals and the resemblances and differences exhibited by the crystals of different substances can be interpreted in terms of the known properties of the chemical elements which make up the crystal. This theory was first advanced by Barlow[b] and Pope[c] and was based upon the assumption that every crystal is a *close-packed* assemblage of atomic spheres which can be partitioned into small cells, all exactly similar and all *marshalled* in rows and columns thus giving the symmetrical form to the crystal. These small cells are the chemical molecules, and the atoms and molecules are assumed to be capable of a certain amount of distortion under the influence of the forces acting between them. This theory has been recently modified and improved by T. W. Richards who introduced the

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[a] Jöns Jacob Berzelius (1779–1848). The son of a school master. Graduated in medicine from the University of Upsala and became a practising physician in Stockholm. In 1806 became Professor of Chemistry in the University of Stockholm. Discovered cerium, selenium and thorium and determined the atomic weights of many of the elements. Introduced the present set of symbols for the elements.

[b] William Barlow (1845–). English Chemist.

[c] William Jackson Pope, F. R. S. (1870–). Professor of Chemistry in Cambridge University.

additional assumption (for which there exists considerable confirmatory evidence from other sources) that the atoms were capable of actual compression as well as distortion. For a more detailed description of this theory and examples of its application to specific cases the student should consult the papers of Richards and of Barlow and Pope cited below. With the assistance afforded by a new system[3] for the quantitative classification of crystals perfected by Federov,[a] the theories of Barlow and Pope and of Richards should mark the beginning of a new epoch in the subject of chemical crystallography.

6. The Internal Structure of Crystals.—A powerful stimulus has recently been given to the old question of the arrangement of the atoms and molecules within the crystal network, by the results obtained from the study of the reflection and refraction of X-rays by crystals. X-rays are now recognized to be of the same nature as ordinary light rays but to have extremely short wave lengths. It occurred to Laue,[b] that if this were the case the successive rows of molecules in a crystal ought to behave toward these very short waves in the same way as a grating spectroscope does to ordinary light rays, that is, diffraction effects and X-ray spectra ought to be obtained. Experiment fully confirmed this conclusion and is not only yielding important information regarding the X-rays themselves but is also giving us pictures of the internal structure of crystals.[6] When X-rays after reflection or refraction by a crystal are allowed to impinge upon a photographic plate or a fluorescent screen, patterns are produced whose form changes as the crystal is rotated in different directions and from a study of the patterns thus obtained, with the crystal held in different positions, the arrangement of the atoms and molecules within the crystal can be determined. In this way it has been found[7] by Bragg and Bragg[c] that in the diamond each carbon atom throughout the whole crystal is surrounded by

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[a] Evgraf Stephanovic Federov, Professor of Mineralogy in the Institute of Mines of the Empress Catherine II, at Petrograd.

[b] Max von Laue, Professor of Theoretical Physics in the University of Zurich, Switzerland.

[c] William Henry Bragg, F. R. S. (1862–). Professor of Mathematics and Physics in Leeds University, England. His son, W. Lawrence Bragg, Investigator in the Cavendish Laboratory, Cambridge, England.

four others so as to form a regular tetrahedron, a discovery which is of much interest to the chemist. This method of investigating crystal structure is still in its infancy but promises to yield many important results.

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JOURNAL ARTICLES: (3) Federov, Z. Kryst. Min., **52,** 11, 22, and 97 (1914). (4) T. W. Richards, Jour. Amer. Chem. Soc., **36,** 382 and 1686 (1914). (5) Barlow and Pope, Ibid., **36,** 1675 and 1694 (1914). (6) W. L. Bragg, *The Analysis of Crystals by the X-ray Spectrometer.* Proc. Roy. Soc. Lon., A, **89,** 468 (1914). (7) Bragg, Ibid., A, **89,** 277 (1914).

CHAPTER VI

CRYSTAL-GAS SYSTEMS

1. Vapor Pressure of Crystals.—If the pressure upon a crystal at constant temperature is gradually reduced, a point will eventually be reached where the gaseous phase appears in the system, that is, the crystal begins to evaporate in much the same way as a liquid does under similar circumstances. The pressure at which the gaseous phase and the crystalline phase are in equilibrium with each other at any temperature is called the vapor pressure or sublimation pressure of the crystals at that temperature. If the processes described in section 7 of Chapter IV be carried out with a crystalline substance, starting at a temperature considerably below its melting point, the character of the isother-

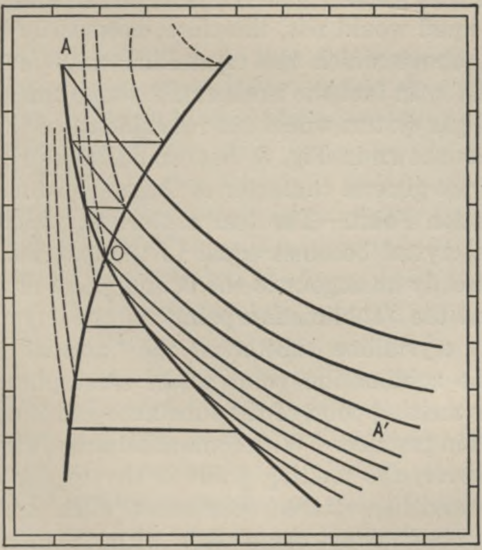

Fig. 10.

mals obtained will at first resemble very closely those of a liquid as shown in Fig. 8. With rising temperature the densities of the two phases, crystalline and gas, gradually approach each other. Long before a temperature is reached where they come very near together, however, the crystalline phase usually melts and thus disappears from the system. We might imagine a case, however, in which the melting point lay at such a high temperature that before it was reached the densities of the two phases became identical. The isothermal for this temperature would then have the same general form as the one marked AOA' in Fig. 10. Identity with respect to density does not, however, necessarily imply that all the other physical properties of the two phases are identical. The temperature at which the densities become equal would not, therefore, necessarily be a **critical temperature,** above which the crystalline state of aggregation could not exist. In fact the isothermals above this temperature in the crystal-gas system would not resemble those for the liquid-gas system, as shown in Fig. 8, but would instead probably be somewhat of the general character of those shown in Fig. 10.

2. Sublimation Point.—The temperature at which the vapor pressure of a crystal becomes equal to the external pressure is evidently perfectly analogous to the boiling point of a liquid and may be called the **"sublimation point"** of the crystal. In the case of most crystalline substances the **"normal sublimation point,"** or the sublimation point under atmospheric pressure, lies above the melting point of the substance and is consequently never reached in practice. With some substances, such as arsenic trioxide, however, the melting point is the higher of the two temperatures and hence these substances when heated simply sublime or "boil" away completely without melting. They cannot be melted except at higher pressures than that of the atmosphere.

3. Heat of Sublimation.—The process of vaporization of a crystal, like that of a liquid, is attended by an absorption of heat and the amount of heat absorbed when one mole of the crystals vaporizes at a given temperature and pressure is called the **molal heat of vaporization** or of **sublimation,** L_S, of the crystals at that temperature and pressure.

CHAPTER VII

CRYSTAL-LIQUID SYSTEMS

1. The Molecular Kinetics of Crystallization and Fusion.—The following hypothetical picture of the mechanism of crystallization and fusion is in accordance with the known facts concerning the process and will help the student to appreciate the probable difference in the molecular condition of the two states of aggregation.

We have already seen (IV, 1) that the molecules of a liquid which have velocities considerably higher than the velocity corresponding to the mean kinetic energy are able to escape from the field of attraction of the other molecules and to enter the vapor phase. There are also present in the liquid numbers of molecules having velocities considerably smaller than this mean velocity. When several of these slowly moving molecules come together the crystal forces, that is, the forces which hold the molecules together in the crystalline state, may be strong enough to prevent the molecules from flying apart again after the impact. These molecules under the influence of the crystal forces may then arrange themselves into the form of a minute crystal which thereafter moves as a unit until it collides with some rapidly moving molecule and is broken up by the impact or else meets with other slowly moving molecules which it attracts and holds, thus growing in size. If heat be gradually and continuously abstracted from the liquid, the temperature falls and the mean kinetic energy of the molecules decreases. This will evidently increase the chances of formation of these minute crystals, called **crystal nuclei,** and will increase their average life and chances of growth. Finally a temperature will be reached at which the mean kinetic energy of the liquid molecules becomes so small that the chances of formation and growth of the crystal nuclei are just equal to their chances of destruction. That is, the chance that any crystal nucleus taken at random will continue to grow by the addition to it of the more slowly moving molecules with which it collides is just equal to the chance that it will be broken up by collision with more rapidly moving molecules.

If the temperature be then further reduced, it is evident that the chances of growth will be greater than the chances of destruction and if a crystal of the substance be now introduced into the liquid and the abstraction of heat be continued, this crystal will be observed to increase in size at the expense of the liquid. In other words the liquid is said to **crystallize** or to **freeze.** If we do not introduce a crystal into the liquid, the crystalline phase may eventually form spontaneously at several points within the liquid. In either case as soon as the crystalline phase appears, it will be noticed that the further withdrawal of heat from the system fails to produce any corresponding decrease in its temperature. It *tends* to cause a lowering in the mean kinetic energy of the molecules of the liquid, it is true, but if the liquid is in contact with the crystalline phase, the slower moving molecules of the liquid are attracted and held by the crystals which thus grow in size at the expense of the liquid phase, the mean kinetic energy in the latter phase and hence also its temperature remaining perfectly constant even though heat be continuously abstracted from it.

Problem 1.—Compare this process with the mechanism by which the temperature of a liquid boiling under constant pressure remains perfectly constant even though heat be continuously added to it.

This constant temperature at which the liquid and crystalline phases are in equilibrium with each other is called the **freezing point** of the liquid or the **melting point** of the crystals.

Let us now consider the reverse process where we start with a crystal at a low temperature and gradually add heat to it. The molecules of the crystal are held in the crystal network by the action of the crystal forces. They are not at rest, however, but oscillate or vibrate about a certain mean position. The plane of oscillation and the amplitude may vary from molecule to molecule but there is probably a mean amplitude of oscillation which like the mean kinetic energy of liquid or gas molecules is dependent upon the temperature. The molecular motion within the crystal is, therefore, unordered, being in all sorts of directions and having all amplitude values on both sides of that average amplitude which corresponds to the temperature of the crystal. The motion is not "free random motion" like that in a gas or a liquid, however, but is instead "restrained random motion" since a molecule cannot move freely about among the other molecules, but can only oscillate about a more or less definite center in the crystal network. From time to time, however, some of the molecules will attain amplitudes of oscillation so great that they will get far enough from the crystal network to escape from the crystal forces and to enter the vapor phase as gaseous molecules. That is, every crystal is able to evaporate and has at each temperature a definite vapor pressure which is the pressure at which the rate of escape of the molecules from the crystal forces is just balanced by the rate at which the gas molecules which are constantly colliding with the crystal are in turn caught and held again by these same forces, thus producing a condition of dynamic equilibrium.

If we gradually impart heat to the crystal, its temperature rises and the rate at which molecules escape from the influence of the crystal forces increases. Finally a temperature will be reached where the crystal breaks up by the above process faster than it can reform and, if the pressure is great enough, the liquid phase appears, that is, the crystal is said to **melt** or to **fuse.** The temperature at which this occurs is the melting point of the substance. It is evident that if the addition of heat is now continued, no further rise in temperature will occur until all the crystalline phase has disappeared since the more violently oscillating molecules in the crystal escape to form liquid molecules and thus the average amplitude of those remaining, and hence also the temperature of the crystal, remains constant, the heat being absorbed by the process of fusion.

2. Heat of Fusion.—The heat absorbed in the process of fusion evidently goes to increase the amplitude of oscillation of the molecules in the crystal to such a value that they can escape from the field of action of the crystal forces. In other words, energy is required to separate them against the action of these forces. A partial mechanical analogy to this process occurs when we whirl a ball at the end of an elastic cord. As we increase its energy of rotation, and hence its angular velocity, the cord stretches and finally when a certain velocity is attained the cord breaks and the ball flies off in a straight line. The heat absorbed in the process of fusion is called the **latent heat of fusion** of the substance and the **molal heat of fusion,** L_F, of any substance at the temperature, T, is defined as the quantity of heat which is absorbed when one mole of the substance changes from the crystalline state at the temperature, T, to the liquid state at the same temperature. It is exactly equal to the quantity of heat *evolved* when the reverse process (crystallization) occurs at the same temperature.

Problem 2.—Suppose we start with a crystal at a low temperature, and at constant pressure gradually add heat to it, measuring the quantity of heat added for each degree rise in temperature which it produces, and continuing the process until we have our substance in the form of vapor at a temperature 100° above its boiling point. If we construct a diagram in which quantities of heat are plotted as abscissæ and corresponding rises in temperature as ordinates, two different diagrams will be obtained according to whether the melting point of the substance is above or below its sublimation point at the pressure employed in the experiment. Draw two figures illustrating the character of the diagrams obtained in the two cases. For simplicity it may be assumed that the substance is not polymorphic.

Problem 3.—If the substance is polymorphic with a transition temperature a few degrees below the melting point, what will be the characters of the above curves?

3. Supercooled Liquids and Amorphous Solids.[1]—The growth of crystal nuclei in a liquid which has been cooled below its freezing point is facilitated by the presence of fine dust particles, by mechanical agitation, and by other factors. In the absence of these aids it is frequently possible to cool a liquid considerably below its freezing point before crystallization occurs. In fact supercooling, as it is called, is the usual phenomenon. A supercooled liquid can usually be caused to crystallize by adding some of its own crystals to it. As soon as crystallization begins the temperature very quickly rises to the freezing point owing to the heat evolved by the process of crystallization.

In all cases a decrease in the temperature of a liquid is accompanied by an increase in its viscosity and with some liquids the viscosity at the freezing point is very large. As the liquid is supercooled the viscosity increases still further. Now high viscosity means decreased freedom of molecular motion within the liquid and molecular motion is necessary for the formation and growth of the crystal nuclei. If this is prevented by a high and steadily increasing viscosity, the liquid may be cooled any distance below its freezing point without any crystallization occurring and the viscosity may finally become so great that the liquid becomes a solid glass. It is still in the liquid state of aggregation, however, for no second phase has appeared during the process of cooling. Ordinary glass is a liquid of this character. These supercooled liquids are sometimes called **amorphous solids** and are distinguished from crystalline solids by the absence both of crystalline structure and of a definite melting point. On heating they gradually soften until they become quite fluid, but there is no one temperature above which they may be called liquid and below, solid, the change in fluidity being a perfectly gradual one. Sometimes old glass gradually and slowly crystallizes. This process is known as devitrification.

Theoretically any liquid could be cooled to a solid glass without crystallization occurring but practically we have only been able to bring this about with the more viscous liquids. Water has been supercooled as much as 80° but was still quite fluid so that when crystallization began it proceeded quite rapidly. If the viscosity of water be increased, however, by dissolving sugar in it, the syrup can be supercooled until it becomes solid and rigid like glass, without the formation of any ice.

When a solid is formed by a chemical reaction in a liquid or gas which is at a temperature far below the melting point of the solid thus produced, the latter frequently appears in the form of a precipitate which under the microscope shows no evidence of crystalline structure. For this reason these precipitates are called **amorphous precipitates.** It is certain, however, that in many instances these solids really belong to the crystalline state of aggregation but that the individual crystals are too small to be seen even with the highest powers of the microscope.

Problem 4.—Describe an experiment which might be made to determine whether an apparently amorphous precipitate were a crystalline solid or a supercooled liquid. (Cf. Problem 2.)

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CHAPTER VIII

RELATIONS BETWEEN PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

1. Nature of the Subject.—Considerable attention has been devoted by investigators to the question of the connection between the physical properties of a substance and its chemical constitution and a large number of relationships have been proposed for expressing quantitatively this connection. Some of the physical properties which have been the subject of investigation in this field are the following: surface tension, viscosity and fluidity, atomic and molecular volume, atomic and molecular heat capacity, heats of fusion, of vaporization and of combustion, melting and boiling points, critical constants, refractivity, dispersive powers, absorption spectra, dielectric constant, magnetic susceptibility and permeability, ionization constants, and penetrating power of the characteristic Röntgen radiations. It would not be possible within the scope of this book to attempt to discuss or even to present more than a very small fraction of the large number of relationships which have been put forward by the different investigators in this field, but the general character of our present knowledge of this subject can be well illustrated by considering two or three typical physical properties and the manner in which they depend upon the chemical constitution of the substance. For this purpose the properties, optical rotatory power, molecular refractivity, and penetrating power of the characteristic Röntgen radiation have been chosen. The consideration of atomic and molecular heat capacities will be taken up later in a special chapter devoted to these properties.

2. Optical Rotatory Power.—When monochromatic light of any wave length is allowed to pass through a Nichol's prism (a special prism made from Iceland spar) the light which emerges from the prism is plane polarized, that is, the light vibrations instead of occurring in all planes are confined to a single plane.

If this light is now examined through a second Nichol's prism (called the **analyser,** the first prism being known as the **polarizer),** with its axis parallel to that of the first prism, the light is apparently not affected. If, however, one of the prisms is now gradually rotated about its axis, the observer notes a gradual decrease in the intensity of the light as seen through the analyser. This decrease continues until complete extinction is reached when the prism has been rotated through an angle of 90° from its first position. If now a solution of some substance such as sugar be placed between the two prisms so that the light passes through the solution, the field of view in the analyser will become illuminated again and in order to produce extinction once more the analyser must be turned through an angle, α, whose magnitude is a measure of the optical rotatory power of the sugar solution. If it is found that the analyser must be turned to the left in order to produce extinction, the optically active substance in the solution is said to be **lævo-rotatory,** while if the rotation of the analyser is to the right, the substance is said to be **dextro-rotatory.** The magnitude of the rotation depends upon (1) the wave length of the light employed, being larger the shorter the wave length; (2) the length of the layer of the solution through which the light passes; (3) the nature of the optically active substance and its concentration in the solution, and (4) the temperature.

The *specific rotatory power*, $[\alpha]$, of a substance is defined by the equation,

$$[\alpha]^{t^\circ} = \frac{100\alpha}{l \cdot p \cdot D} \tag{1}$$

where α is the angular rotation observed when a solution containing p per cent. of the substance and having the density, D, is examined through a tube of length, l, at the temperature, t. The nature of the monochromatic light employed is usually indicated by a subscript. Thus $[\alpha]_D^{20^\circ}$ indicates that the value is for 20° C. and that the D-line of the sodium spectrum was employed as the monochromatic light. The specific rotatory power of a substance is in general a function both of the temperature and of the nature of the solvent in which it is dissolved.

The property of optical activity is closely and uniquely connected with the chemical structure of the molecule of the optically active substance. It occurs in the case of every substance whose molecule contains an asymmetric central atom (see I, 2d, which should be re-read in this connection) and also in nearly all cases in which the tetrahedral space model of the molecule possesses no plane of symmetry. The quantitative side of the relation between optical activity and molecular structure is not very well developed at present although the measurement of the specific rotatory power of a substance can in certain cases be employed to determine the structure of its molecule or to decide which of two possible structures is the correct one.[2]

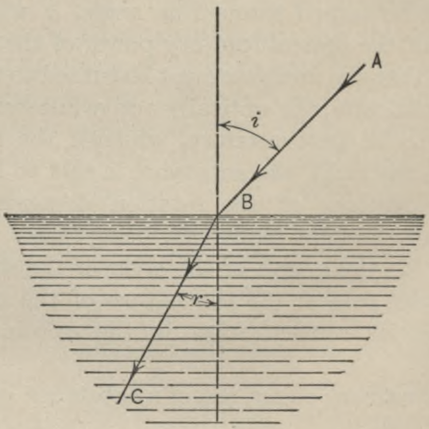


FIG. 11.

3. Molecular Refractivity.—When a ray of light passes from one medium into another (from air into water, for example) the ray undergoes a change in direction, that is, it is refracted. The angle made by the incident ray (AB, Fig. 11) with a perpendicular at the point of incidence is termed the angle of incidence, i, while that, r, made by the refracted ray (BC in the figure) is termed the angle of refraction. The **index of refraction,** n, of a substance is defined by the equation

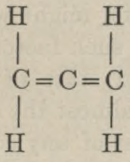
$$n=\frac{\sin i}{\sin r}=\frac{u_1}{u_2} \qquad (2)$$

where light of a single wave length is supposed to enter the substance from a vacuum, the velocity of the light in the vacuum being u_1, and that in the substance being u_2. In practical work air may usually be employed instead of a vacuum. For a given substance the relation, $\frac{n^2-1}{n^2+2}\times\frac{1}{D}$, where D is the density, has been found to be a constant independent of the temperature. This is known as the **Lorenz[a]-Lorentz[b] relation.**

The **molecular refractivity,** $\frac{n^2-1}{n^2+2}\times\frac{M}{D}$, where M is the molecular weight, has been found to be an additive property in the case of many organic liquids; that is, to each element a definite atomic refractivity can be assigned and from these values the refractivity of a compound of the elements may be calculated. More extensive studies, however, show that not only the nature of the elements in the compound but the arrangement of the atoms in the molecule must also be taken into account. Thus the molecular refractivities of the two compounds,

$$H-C\equiv C-C\equiv H_3$$

and



$$\begin{array}{ccccc} H & & & & H \\ | & & & & | \\ C & = & C & = & C \\ | & & & & | \\ H & & & & H \end{array}$$

will not be the same even though they have the same atomic composition. Account must be taken of the fact that one molecule contains single and triple bonded carbon atoms while the other contains only single and double bonded carbon. Further investigations have shown that the positions of the atoms in the molecule with respect to one another and to double or triple bonds also exert an influence upon their atomic refractivities, so that the whole question becomes a very complicated one. When employed with care, however, the measurement of the refractive index of an organic liquid may be and frequently has

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[a] L. Lorenz, Formerly in the University of Copenhagen.

[b] Hendrick Anton Lorentz, Professor of Physics in the University of Leyden.

been of considerable value in determining its chemical constitution. This same statement holds in varying degrees with reference to many other physical properties.

The extent to which a given physical property of an element in a compound is affected by the natures of the other elements with which it is combined and by the manner in which its atoms are united with those of the other elements to form the molecule of the compound will obviously depend upon what characteristic of the element is chiefly operative in determining the magnitude of the property in question. Thus, if the property is one whose magnitude depends upon the shape or the size of the atom or upon the nature of its motion in space, or if it depends upon the positions, number, or movements of the electrons in or near the surface of the atom, then it is not difficult to understand why the property in question will be affected by chemical constitution, for each of the factors mentioned might easily be affected by the influences of the neighboring atoms in the molecule. Only in the case of physical properties which are practically entirely determined by conditions within the core of the atom and thus removed from the influence of external conditions surrounding the atom, might we expect to find properties which are not affected by such factors as chemical constitution, pressure, temperature and state of aggregation. Mass is, of course, the principal and almost the only strictly **additive property,** that is, the total mass of any compound is always the sum of the masses of the elements which entered into reaction to form the compound, irrespective of the structure or composition of this compound. Nearly all other physical properties are **constitutive properties** to a greater or less degree depending upon the nature of the property. A recently discovered property, however, seems to resemble mass in being unaffected by any external conditions surrounding the atom. We shall consider this property briefly.

4. Penetrating Power of the Characteristic Röntgen Radiation of an Element.—When Röntgen[a] rays (X-rays) are allowed to fall upon a substance the substance in turn is caused to emit

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[a] William Conrad Röntgen, F. R. S. (1845–). Professor of Experimental Physics in the University of Munich. The discoverer of X- or Röntgen Rays.

secondary Röntgen rays whose penetrating power seems to be determined solely by the nature of the elements in the emitting substance. In the accompanying table (Table XIII) are shown the results of a series of measurements of the penetrating power of the characteristic Röntgen radiation of the element bromine in different compounds. The character of the emitted rays evidently appears to be quite unaffected by the chemical or physical condition of the element. Similar measurements with the element iron show that its characteristic Röntgen radiation is the same at room temperature as it is at red heat and is identical from ferrous and from ferric compounds. The penetrating power of this characteristic radiation increases gradually and continuously with increasing atomic weight of the emitting element being too small to be measured in the case of the elements with atomic weights less than 24. Unlike most of the physical properties of the elements this property is, therefore, *not* a periodic function of the atomic weights. Its complete independence of external conditions surrounding the atoms indicates strongly that it is closely connected with the nature of the cores of the atoms giving rise to it.

TABLE XIII

Illustrating the penetrating power of the characteristic Röntgen radiation of the element bromine in different chemical compounds and in different states of aggregation (Chapman, Phil. Mag., **21,** 449 (1911)).

Previous per cent. absorption by Al	Per cent. absorption by Al (0.0062 cm. thick)		
	Radiation from		
	C_2H_5Br vapor	NaBr solid	BrOH solid
0	24.1	24.8	24.0
24	24.4	24.3	24.5
42	24.1	23.4	24.2
75	24.7	23.6	....

Within the last year (1913–14) a more exact study of the nature of characteristic Röngten radiations has become possible through the employment of crystals as spectrometer gratings, (V, 6) and in this way Moseley[3] has found that the spectrum of the characteristic radiations is extremely simple, being composed of very few lines. The frequencies corresponding to these lines, moreover, are closely connected with the positions of the elements in the periodic system and investigations in this field are giving us a new insight into the significance of the periodic system and the relations of the elements to one another.[4] These relationships will receive detailed consideration in a later chapter. (Chapter XXVII.)

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CHAPTER IX

THE BROWNIAN MOVEMENT AND MOLECULAR MAGNITUDES

1. The Brownian Movement.—In order to account for the known behavior of material bodies, they were early assumed (I, 1) to be made up of very small particles called molecules which were in a state of very rapid and constant unordered motion. The examination of a pure substance, a drop of liquid for example, with the highest powers of the best modern microscope fails to reveal the presence of any such rapidly moving particles, however, and hence, if the liquid is made up of such particles, they must be so small as to be beyond the range of our most powerful microscopes. How could the presence of these rapidly moving molecules be rendered visible?

Suppose we were to stir into a liquid some insoluble substance in an exceedingly fine state of division, the particles of which were in fact so small that their presence in the liquid could barely be detected with the microscope. Now if the liquid is in reality composed of molecules moving to and fro in all directions with the enormous velocities assigned to them by the molecular theory (see II, prob. 2), then it is clear that the collisions of the rapidly moving molecules with these small visible particles (called **colloidal particles**) ought to set the latter into motion also and through a properly arranged microscopic system one should be able to observe and study the motion of these colloidal particles. The presence of visible particles possessing an irregular motion was noticed in 1827 by Robert Brown, an English botanist while examining with the microscope a liquid containing some pollen grains. The cause of this irregular motion, called from its discoverer the Brownian Movement, was not suspected until a number of years later, however. The researches[2] of Wiener (1863), Ramsay (1876), Delsaulx and Carbonelle (1880), Gouy (1888), and others demonstrated that the movement could not be due to convection currents in the liquid, that it was nearly independent of the nature of the colloidal particles, that it was more rapid the smaller the particles and the less viscous the liquid, and that it was persistent and never changing, continuing day and night, month after month. It has in fact been observed in small quantities of liquid found in little pockets in granite and other rocks where it must have been shut up for millions of years. All of these facts pointed to the theory first suggested by Wiener that the Brownian Movement is the result of molecular motion within the liquid. In other words the small visible colloidal particles are knocked about by colliding with the invisible molecules like foot balls in the midst of a crowd of invisible players.

2. The Distribution of Colloidal Particles under the Influence of Gravity.—A liquid containing colloidal particles is called a "colloidal solution" and if such a solution is kept undisturbed at a constant temperature for some time, the colloidal particles are found to be distributed so that the density of their distribution is greatest near the bottom of the vessel and decreases with height. This is a similar behavior to that shown by the atmosphere as one rises above the surface of the earth and Einstein[a] showed that, if the Brownian Movement is caused by molecular motion, the distribution of the particles with height must follow quantitatively the law which governs the decrease in density of the atmosphere with height. This law can be readily derived from the perfect gas law and may be expressed as follows:

$$\log_e \frac{D_1}{D_2} = \frac{Mg(h_2 - h_1)}{RT} \tag{1}$$

where D_1 and D_2 are the densities of air at the heights h_1 and h_2 respectively, M is the molecular weight of air (II, 12), g the acceleration due to gravity, R the gas constant, and T the absolute temperature.

Problem 1.—Derive the above equation from the perfect gas law assuming T to be independent of h.

For the molecular weight M we can put

$$M = m\mathbf{N} \tag{2}$$

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[a] Albert Einstein, since 1914, Professor of Theoretical Physics at the University of Berlin. Formerly at the University of Zurich.

where m is the mass of one molecule (or colloidal particle) and $\mathbf{N}$ is Avogadro's number (I, 6) and in the case of the colloidal solution, for m we can put,

$$m = VD = V(D_c - D_l) \qquad (3)$$

where V is the volume of the colloidal particle, and D, its "density in the solution," is equal to its absolute density, D_c, minus the absolute density, D_l, of the liquid in which it is suspended. We thus obtain the relation

$$\log_e \frac{D_1}{D_2} = \log_e \frac{n_1}{n_2} = \frac{\mathbf{N}V(D_c - D_l)g(h_2 - h_1)}{RT} \qquad (4)$$

where n_1 and n_2 are the average number of colloidal particles in any given volume at the heights h_1 and h_2 respectively.

Perrin[a] was able to determine the numbers, n_1 and n_2, by photography (see Fig. 12) and by direct count, and the difference in level, $h_2 - h_1$, could be read directly from the micrometer screw of the microscope. Since for a given colloidal solution the other quantities in equation (4) are constants, Perrin was thus able to make a quantitative test of the equation. In this way he found in one experiment[2] that the number of particles at four different levels were in the ratios, 116, 146, 170 and 200, while the values calculated from equation (4) for the same levels were 119, 142, 169 and 201. Numerous other experiments gave similar results thus confirming quanti-

FIG. 12.—Micrographs of a colloidal solution of mastic at three different levels 12μ apart. (Perrin, J. Phys., Jan. 1910, p. 24.)

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[a] Jean Perrin, Professor of Physical Chemistry at the Sorbonne, Paris.

tatively the theory that the Brownian Movement is the result of molecular impacts.

But Perrin was able to go further than this. By means of fractional centrifugation he was able to prepare uniform colloidal particles of gamboge and of mastic of any desired size. He was also able to measure the diameter and hence the volume of the individual particles by several different methods which gave concordant results. Knowing the volume of the particles it is clear that equation (4) can be employed to calculate a value for **N**, Avogadro's number. For this purpose Perrin conducted a set of experiments in which the volume of the particles employed was varied fifty-fold, the density of the suspending liquid fifteen-fold, and its viscosity 250 fold in the different experiments.

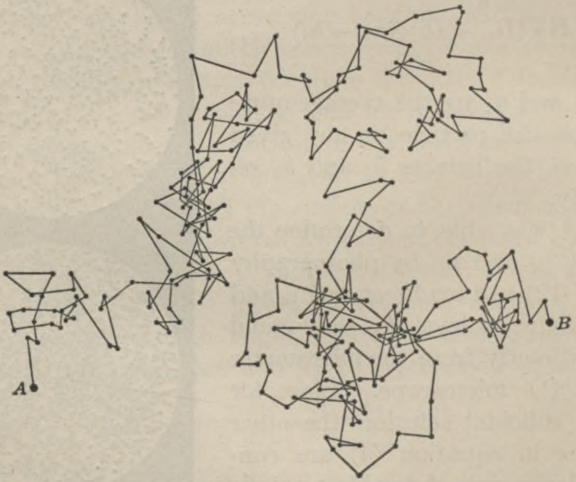

FIG. 13.—Path of a colloidal Particle. (Reproduced from *Les Atomes* by J. Perrin.)

From all of these experiments, however, substantially the same value, $6 - 7 \times 10^{23}$, was obtained for **N** and this is the value which is found for this constant by a number of entirely different methods, again furnishing a strong quantitative confirmation of the theory of the cause of the Brownian Movement.

3. The Law of the Brownian Movement.—If a given colloidal particle be watched under the microscope it will be found to move through a very irregular and complicated path. Fig. 13 shows the horizontal projection of the path of a colloidal particle which occupied the position A at the beginning of the observation and which had reached the position B, t minutes later, having meanwhile occupied successively all the positions indicated by the small dots. The distance from A to B in a direct line is called the *horizontal displacement*, X, of the particle in the time t, and is determined by the energy of agitation of the particle and the resistance offered to its motion by the viscosity of the suspending liquid. Einstein was the first to derive the quantitative expression for the displacement of a colloidal particle. On the assumption that the Brownian Movement was the result of the impacts of the molecules of the liquid with the colloidal particles he showed[1] that for a large number of observations the average value of the square of the horizontal displacement (X^2) of a spherical colloidal particle in the time t ought to be

$$X^2 = \frac{RT}{\mathbf{N}} \frac{t}{3\pi r\eta} \tag{5}$$

where r is the radius of the particle and η the viscosity of the medium. In deducing this relation Einstein also assumed that the motion of the particle under a constant force f took place in accordance with Stokes'[a] Law, that

$$u = \frac{f}{6\pi r\eta} \tag{6}$$

where u is the velocity of the particle.

Equation (5) was tested by Perrin using his colloidal solutions of gamboge and mastic. He was able to show that the motion of the particles obeyed Stokes' Law and that the proportionality between X^2 and t required by the equation of Einstein was also fulfilled. From his measured values of X^2 he computed the value of **N** by means of Einstein's equation with the following very striking results:[1]

[a] George Gabriel Stokes, Kt., F. R. S. (1819–1903), Lucasian Professor of Mathematics at Cambridge University. Author of many important contributions to hydrodynamics and optics.

Character of solution	Radius of the particles in μ	Mass of the particles $m \times 10^{15}$	Number of observed displacements	$\mathbf{N} \times 10^{-23}$
Gamboge in water...........	0.50	600	100	8.0
	0.367	246	1500	6.9
	0.212	48	900	6.9
Gamboge in a 35 per cent. solution of sugar (temperature poorly defined).	0.212	48	400	5.5
Mastic in water.............	0.52	650	1000	7.3
Mastic in a 27 per cent. solution of urea.	5.50	750,000	100	7.8
Gamboge in a 10 per cent. glycerine solution.	0.385	290	100	6.4

It will be noticed from the table that the equation of Einstein holds fairly well even for such large variations in mass as 15,000-fold. Perrin considers the value $6.9 \cdot 10^{23}$ to be his most reliable one.

More recent investigations by Nordlund in the laboratory of Svedberg[a] at Upsala give a somewhat lower value. Nordlund employed a colloidal solution of mercury, the perfectly spherical particles of which had a radius of 3μ. His apparatus was arranged so that the motion of the particles was recorded automatically upon a moving photographic film, thus eliminating any errors due to personal judgment concerning the path of the particle under observation. Nordlund's experiments showed that the value of X^2 was directly proportional to the time, as required by Einstein's equation (see Fig. 14) and he also found by independent experiments that the tiny spheres of mercury obeyed Stokes' law. Nordlund's experiments are probably the most trustworthy ones upon which to base a calculation of **N** from the Brownian Movement in liquids. He found[5] as a mean value from twelve experiments $\mathbf{N} = 5.9 \times 10^{23}$, the average deviation of

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[a] Theodor Svedberg, Professor of Physical Chemistry at the University of Upsala.

the individual values from this mean being 10 per cent. It seems therefore safe to conclude that from the study of the Brownian Movement in liquids, we find the value of Avogadro's Number to be **N** = $(5.9 \cdot 10^{23} \pm 10$ per cent.).

4. The Brownian Movement in Gases.—Owing to the comparative simplicity of conditions in the gaseous state (XI, 3*a*) the determination of the value of **N** from the study of the Brownian Movement in gases offers fewer difficulties than in the case of liquids. Because of the greater distances separating the molecules of a gas, the collisions between the colloidal particles and the molecules are less frequent and the mean free paths (III, 2) of the colloidal particles are, therefore, much longer than in liquids. Thus the average displacement of a given colloidal particle in a given time is increased 130-fold by transferring the particle from water to air at 1 mm. pressure.

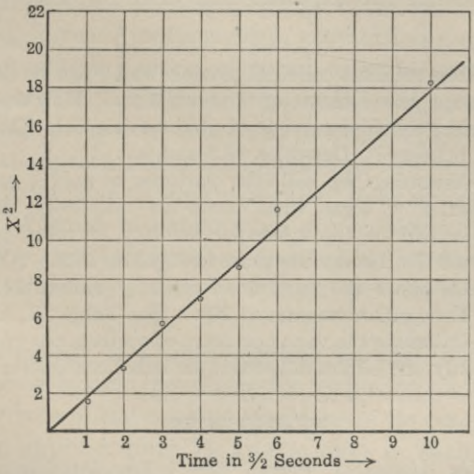

FIG. 14.—Illustrating the proportionality between time and the square of the horizontal displacement of a colloidal particle, as required by Einstein's equation. (Nordlund, Z. physik. Chem., **87,** 59 1914.)

The most accurate study of the Brownian Movement in gases has been carried out by Millikan and Fletcher at the University of Chicago. They employed a tiny drop of oil as the colloidal particle. Such a drop when watched through a telescope is seen to dart rapidly about to and fro in all directions and forms a very vivid picture of the motion of the invisible gas molecules through collision with which it is knocked about in this rapid and irregular fashion. From a large number (5900) of measurements of the displacements along one axis of 12 such particles, Fletcher has very recently[7] obtained the value, **N** = $(6.03 \times 10^{23} \pm 1.2$ per cent.) for Avogadro's constant.

The accurate value $(6.062 \cdot 10^{23} \pm 0.25$ per cent.) for **N** given in Chapter I was obtained by Millikan[a] by an entirely different experimental method which will be described in Chapter XVI, 6. It will be noticed that the two most reliable values for **N** yielded by the Brownian Movement method agree with the above more exact value within the experimental error of their own determination.

Problem 2.—The smallest colloidal particle which can be detected under the ultramicroscope has a diameter of about 3 $\mu\mu$. How many atoms are there in a spherical colloidal particle of gold having this diameter? How many in one of benzene? Densities 19.5 and 0.9.

Problem 3.—Assuming the colloidal particles of gold 3 $\mu\mu$ in diameter to be the "molecules" of a gas, what would the "molecular weight" of this gas be? What would be the molecular velocity, in miles per second, of these molecules at 0°? The specific gravity of gold is 19.5. (Cf. II, prob. 2.)

Problem 4.—Calculate the number of mercury molecules in one cubic centimeter of a Torricellian vacuum at 20°. (See Table IX, Chap. IV.)

Problem 5.—Calculate the vapor pressure of a substance whose saturated vapor contains only one billion molecules per cubic centimeter at 20°.

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[a] Robert Andrews Millikan (1868–). Professor of Physics in the University of Chicago.

CHAPTER X

SOME PRINCIPLES RELATING TO ENERGY

1. Energy.—Energy as a concept may be defined as the agency postulated by science as the underlying cause of all changes which we observe in the properties, or condition of any portion of the material universe. In accordance with the conditions under which it manifests its presence, energy is usually classified under the following forms: kinetic energy, gravitation energy, cohesion energy, disgregation energy, electrical energy, magnetic energy, chemical energy, radioactive energy, heat energy, radiant energy, etc. We shall not stop at this point to explain just what is meant by each of these terms as the explanations can be more conveniently given from time to time as we shall have occasion to employ the terms. A word of explanation is necessary, however, with regard to the term **potential energy** which we shall have occasion to employ in connection with the kinetic energy of molecular motion.

Potential energy is usually defined as the energy which an elastic body or system possesses by virtue of its configuration, that is, by virtue of the relative positions of its component parts. Thus, if we apply a force to any system in such a way as to gradually and continuously change its configuration, using only the force necessary to bring about the desired change, we are said to do **work** upon the system. If the system is a perfectly elastic one, that is, if it will *of itself* on removal of the impressed force return completely to a configuration which as far as its energy is concerned is identical with its original configuration, then it is capable, in so returning, of doing an amount of work exactly equal to that expended in changing it from its first to its second configuration. In the second configuration, therefore, it is said to possess **potential energy** because it has a tendency *of itself* to change to another configuration as soon as the restraint upon it is removed, and in so changing is capable of performing a definite amount of work. Its potential energy in configuration 2 is quantitatively defined as equal to the work which the system is capable of performing in changing from configuration 2 to configuration 1.

The following examples will serve to illustrate the concept of potential energy. A steel rod bent or twisted under tension, a stretched rubber string, and a compressed fluid, are all examples of systems possessing potential energy. A system composed of the earth and a stone held at any position above the surface of the earth also possesses potential energy, for, if the stone is allowed to fall, it is capable of doing a definite amount of work before it reaches the surface of the earth. If a stone of mass, m, be thrown directly upward by the action of some force, it starts with an initial velocity u_1, and, therefore, possesses an initial kinetic energy, $\frac{1}{2} mu_1^2$. As it rises its velocity steadily decreases until it finally becomes zero. Its kinetic energy also becomes zero at the same time. The system composed of the stone and the earth is, however, now said to possess an amount of potential energy exactly equal to the initial kinetic energy of the stone, for in falling to the earth the stone will again acquire the kinetic energy, $\frac{1}{2} mu_1^2$. Loss of kinetic energy in this case is accompanied by the gain of an exactly equivalent quantity of potential energy, the sum of the two remaining always the same. More generally stated, the capacity of the system for performing work is always the same whatever be the position of the stone, until it has returned once more to the surface of the earth and its kinetic energy is converted into heat.

2. The Nature of Heat Energy.—If two perfectly elastic bodies, two molecules of a monatomic perfect gas such as helium for example, collide with each other, the total kinetic energy possessed by the two bodies is not changed by the collision. When a monatomic perfect gas is heated, therefore, the heat which it absorbs should all be used up in increasing the kinetic energy of translatory motion of the molecules of the gas. This conclusion is in perfect accord with the experimental facts concerning the specific heat of monatomic gases. The total heat content of a mass of a monatomic perfect gas containing n molecules would, therefore, be $\frac{1}{2}nmu^2$, where $\frac{1}{2}mu^2$ is the mean translatory kinetic energy of the molecules.

If the gas is di-, tri-, or polyatomic, however, this would not necessarily be the case, for in a collision between two such molecules some of the energy of the collision might go to increasing the distances separating the atoms within the molecule and would thus be doing work against the forces holding the atoms in their positions or orbits. The corresponding increase in the intra-molecular energy would be classed as an increase in intra-molecular *potential* energy because it is regarded as existing by virtue of the new configuration of the molecule. An increase in intra-molecular kinetic energy might also occur because some of the energy of the collision would probably go to increasing the vibration or oscillation of the atoms within the molecule. Similarly when heat is absorbed by a liquid, a crystal, or a compressed gas, part of the energy may be used up in doing work against internal forces acting between molecules or between atoms within molecules. It therefore becomes inter- or intra-molecular potential energy. When heat is abstracted from such a body by thermal conduction this inter- and intra-molecular potential energy is first transformed into unordered molecular kinetic energy and is then given up to the surroundings. Hence as far as our purposes are concerned this molecular potential energy acts like a reservoir of molecular kinetic energy since it is not accessible to us except by previous transformation into unordered molecular kinetic energy.[1] Viewed from the standpoint of its availability for purposes of doing useful work, therefore, any form of energy may be, and in fact must be, classed with heat energy if it is of such a nature that we are not able, even in principle, to abstract it from a system until it has first been converted into unordered molecular kinetic energy or unordered vibratory radiant energy.

The quantity of heat energy which must be imparted to one gram of any pure substance in order to raise its temperature one degree without change of state is called the **specific heat capacity** of the substance and the product of the specific heat into the molecular or atomic weight is called the molal (or molecular) heat capacity or the atomic heat capacity. The subject of specific heats will be considered more in detail in a later chapter.

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[1] Or unordered vibratory motion in the ether in case it is transmitted from the body by radiation.

3. The First Law of Thermodynamics.—We have just seen that the heat content of a body or system of bodies arises from the kinetic and potential energy possessed by its moving atoms and molecules. In addition to its content of heat energy a system may, of course, contain energy in other forms (chemical or electrical, for example) and the total amount of all forms of energy which any system contains is called its **total energy** or its **internal energy** and is represented by the letter *U*. We know nothing as to the magnitude of the **total energy** of any system but when any change takes place in a system there is usually a corresponding **change** in its total energy, either a decrease due to its giving up some of its energy to the surroundings or an increase through receiving energy from the surroundings. These **changes** in the total energy of a system we are able to study and to measure, and experience has shown that they obey the following law, known as the law of the conservation of energy or the **First Law of Thermodynamics: When a quantity of energy disappears at any place a precisely equivalent quantity appears at some other place or places; and when a quantity of energy disappears in any form a precisely equivalent quantity simultaneously appears in some other form or forms.** In other words energy can neither be created nor destroyed. Two quantities of energy are said to be equivalent if, when converted into the same form (heat, for example), they yield identical amounts of that form. Thus if a certain amount of radiant energy be entirely absorbed by 1 gram of water with the result that the temperature of the water rises 1°, the amount of radiant energy is equivalent to 1 calorie of heat energy. If a certain quantity of electricity flows through a coil of wire immersed in one gram of water and thereby produces a rise of one degree in the temperature of the water, the electrical energy is equivalent to one calorie of heat energy, and the quantities of radiant energy and of electrical energy involved in these two experiments are, therefore, equivalent to each other.

It has been found convenient to divide the change in total energy which accompanies any process taking place within a system into two classes, designated as heat, *Q*, and work, *W*, respectively. The reason for this division lies in a practical difference between heat energy, on the one hand, and all other forms of energy on the other hand, which difference is the cause of a certain restriction upon our ability to transform heat energy into other forms of energy. This difference is due to the fact that in the case of heat energy (and in this class are included certain forms of radiant energy) the motion of the moving parts is unordered, or random motion, while in the case of all other forms of energy involved in any process of energy transformation or transference the movement of the parts whose motion gives rise to the energy in question is **ordered** motion, that is, it is directed in one or two or at most a few definite directions, instead of having the random character of molecular motion.

On the basis of the above classification of energy it follows from the conservation law that when any process takes place within a system, the corresponding change in the total energy of the system must be made up of the work of the process and the heat of the process, or more exactly stated, the **increase,** ΔU, in the total energy, U, of any system, which occurs when any process or change takes place within the system, is equal to the quantity of heat, Q, **absorbed by** the system **from** the surroundings, diminished by the quantity of work, W, done **by** the system **upon** the surroundings, or in mathematical language,

$$\Delta U = Q - W \tag{1}$$

This equation is the mathematical formulation of the **First Law of Thermodynamics.**

The following example is an illustration of its application to a specific process: If a mixture of hydrogen and oxygen in a cylinder provided with a weighted piston is exploded, the force of the explosion will raise the weighted piston through a certain distance against the force of gravity and there will be a simultaneous evolution of heat which will be gradually taken up by the surroundings. Suppose the weight lifted to be 10,000 grams and that it is raised 10 meters. The work done upon it would be 10,000×1000×980 ergs, where 980 (dynes) is the acceleration due to gravity. This is 9,800,000,000 ergs or 980 joules and is evidently work done **upon** the surroundings **by** the system since it is done against a force, gravitation, exerted by the surroundings upon the weighted piston. Since one calorie is equivalent to 4.2 joules, the above quantity of work is equivalent to $\frac{980}{4.2}=233$ calories. Suppose that the heat **evolved** by the explosion is 1000 calories. The quantity, Q, therefore, in equation (1) would be -1000 calories, since Q has been so defined as to be **positive** when heat is **absorbed by** the system **from** the surroundings. For the increase, ΔU, in the total energy of the system which results from the above process we have, therefore,

$$\Delta U = Q - W = -1000 - 233 = -1233 \text{ cal.}$$

or, in words, the total energy of the system has **decreased** by 1233 calories, since the value of ΔU comes out with a negative sign. The above example of the application of the equation of the First Law brings out the fact, which the student should always keep in mind, that *before two energy quantities can be employed together in an equation they must first be expressed in terms of the same energy unit.*

4. Corollaries of the First Law.—A little consideration will show that the following two statements are necessary consequences of the First Law of Thermodynamics:

1. The total energy of any system in a given state or condition is, for the system in question, a definite characteristic of that state and is independent of the manner in which the system reached that state.

2. When a system changes from a state, A, where its total energy is U_A, to some other state, B, where its total energy is U_B, the increase in total energy, $\Delta U = U_B - U_A$, which accompanies this change is independent of the process by which the change is brought about.

For example, one gram of the substance, water, in the form of ice at a temperature of $-10°$ and a pressure of one atmosphere contains a definite amount of energy which is the same for every gram of water in this condition irrespective of the previous history of the water provided it has been in this condition for sufficient time to reach a state of equilibrium. If we wished to convert a gram of water in the above condition into one gram of water vapor at a temperature of 200° and a pressure of one-tenth of an atmosphere, we could do so in a variety of different ways. For example, we might first reduce the pressure upon the ice until it had all evaporated and then the vapor could be heated to 200° and the pressure brought to one-tenth of an atmosphere; or, we might first melt the ice, heat the resulting water to boiling, boil it all away and then heat the steam to 200° and bring the pressure to one-tenth of an atmosphere; or, we could dissolve the ice in an aqueous solution of sulphuric acid and pass a current of electricity through this solution between platinum electrodes, until one gram of a mixture of hydrogen and oxygen gases were evolved. This mixture could then be exploded and the water vapor formed could be cooled to 200° and the pressure upon it brought to one-tenth of an atmosphere. By whatever process the above change is brought about, however, we should find that the total energy change accompanying the process is always the same irrespective of the nature of the process.

5. Work and Energy Units.—The work associated with any process may always be regarded as ordered motion taking place under the influence of a force, f, and when so regarded, is quantitatively defined as the product of the force into the distance through which it acts. On the basis of this definition it can be readily shown that in the case of a change in the volume of a system against a pressure, the work *done by* the system is equal to the product of the *increase* in volume, Δv, and the pressure, p, under which it takes place or, for an infinitesimal volume increase, we have

$$\mathrm{d}W = p\mathrm{d}v \tag{2}$$

If the pressure is constant during the change in volume, the integral of this expression is

$$W = p(v_2 - v_1) = p\Delta v \tag{3}$$

where v_1 and v_2 are the initial and final volumes, respectively. If the pressure is expressed in atmospheres and the volumes in liters, the corresponding energy unit is called the **liter-atmosphere,** one liter-atmosphere being defined as the work done when a volume increase of one liter occurs against a constant pressure of one atmosphere.

In the case of electrical work our definitions of electrical quantities are such that the electrical work done when a current of electricity flows under a difference of potential is equal to the quantity, q, of electricity multiplied by the difference of potential, E, under which it flows. If the quantity of electricity is expressed in coulombs and the potential difference in volts, the product will be **volt-coulombs** or **joules.**

Work, heat, or any form of energy may, of course, be expressed in any one of the various energy units, ergs, joules, calories, or liter-atmospheres. The definitions of the various units have already been given in the Introduction. They are related to one another quantitatively by the following equations:

1 liter-atmosphere = 24.207 cal.
1 cal. = 4.184 joules
1 joule (by definition) = 10^7 ergs.

6. The Relation Connecting Heat of Fusion, Heat of Vaporization, and Heat of Sublimation.—

Problem 1.—Prove that the First Law of Thermodynamics requires that the molal heat of fusion (L_F), of vaporization—of the liquid—(L_v), and of sublimation (L_s), in the case of any substance shall be connected by the equation,

$$L_s = L_F + L_v \tag{4}$$

provided all of the processes mentioned occur at the same constant temperature, T, and pressure, P.

Problem 2.—In order to melt one gram of ice at 0° and a pressure of one atmosphere 79.60 calories of heat are required. To convert 1 gram of water under the same conditions into saturated vapor requires 2494.6 joules of energy. How many calories of heat will be evolved during the deposition of 18 grams of hoar frost from saturated air at 0°?

7. The Second Law of Thermodynamics.—With respect to the transformation of work into heat (that is, of ordered or directed motion into unordered or random molecular motion) our experience teaches us that there is no restriction except that contained in the First Law of Thermodynamics which merely requires that in such a transformation the amount of heat produced shall be exactly equivalent to the work expended, or in other words that there shall be neither destruction of energy nor creation of energy out of nothing. But with respect to the reverse transformation of heat into work (of random molecular motion into directed motion of some kind), our experience teaches us that there are certain practical restrictions imposed by nature in addition to those contained in the statement of the First Law.

The complete statement and description of the nature of these restrictions comprises what is known as the Second Law of Thermodynamics.

That some additional restriction is perhaps to be expected, knowing as we do the random nature of the motion which gives rise to heat energy, will be appreciated from the following considerations: In the case of a moving mass large enough for us to control it as an individual we can theoretically convert all or any part of its kinetic energy into some other form of useful energy, or in other words, can make it do any desired form of work. In the case of a moving molecule, however, the moving body is too small for us to control its motion as an individual. We can see, therefore, at once that, as far as we are concerned, the kinetic energy of such a small particle as a molecule is not available for our uses in the same sense as that of a body large enough for us to control as an individual. Suppose, however, that we have a very large number of small particles all moving in the same direction, or of whose motion there is a sufficiently large component in some one direction. We have such a situation, for example, in a metallic wire through which a current of electricity is passing. The current consists of a stream of electrons (I, 2g) which at any moment are all moving in one direction through a given cross section of the wire, or at least the motion of every electron has a positive component in this direction. In such a case the particles are likewise too small to be controlled as individuals but they have a resultant kinetic energy in one direction which is large enough for us to control and we are thus able to transform this energy into some desired form of useful work.

In the case of heat energy, however, we are dealing with a very large number of particles, too small to be controlled as individuals, and whose motion is perfectly at random; that is, if we were to resolve the motion of all the molecules of a gas or a liquid in any direction whatever, the resultant motion and hence also the resultant kinetic energy in this direction for any finite interval of time would be zero, as far as our purposes are concerned. In order, therefore, to convert unordered molecular kinetic energy into ordered kinetic energy, that is, in order to transform heat into work, we are obliged to slow up *all* of the moving molecules, or in other words, to reduce their average kinetic energy and hence to lower the temperature of the body from which we wish to take the heat energy.

For example, when a gas expands and raises a weight it does work, but in doing so it always *cools off*, that is, the average kinetic energy of its molecules decreases, the total decrease in the molecular and atomic kinetic and potential energy being exactly equivalent to the work done. If the gas is kept in a large heat reservoir during its expansion, it will take up heat from the reservoir which in turn will cool down. That is, the heat energy necessary for performing the desired work will come from the reservoir instead of from the gas itself, and, if the heat reservoir is large enough in comparison with the amount of gas employed, the amount by which it is cooled down will be infinitesimal, since the decrease in molecular energy will be distributed over such an enormous number of molecules that the average kinetic energy of each molecule and hence the temperature of the reservoir would remain practically unaltered. For practical purposes, therefore, we may regard a compressed gas in good thermal contact with a sufficiently large heat reservoir (such as the ocean, for example) as a device for converting the heat energy of the reservoir into useful work at *practically* constant temperature and as long as our supply of compressed gas lasted we might go on converting heat into work in this manner. Large supplies of compressed gas are not available, however, and if we attempted to compress the gas after expansion with the idea of using it over again, we would find that, even under the most theoretically perfect conditions, it could not be compressed to its original pressure except by the expenditure of at least as much work as could be obtained from it during the expansion described above. Practically we would always find that more work would be required. In other words the operation could not be worked in **a cycle** for the purpose of transforming heat into work. In fact all of our experience leads to the conclusion that:

A system or arrangement of matter operating in a cycle cannot transform heat into work in surroundings of constant temperature. This statement evidently constitutes a restriction upon the transformation of heat into work and is part of the Second Law of Thermodynamics. The rest of the law has to do with the transformation of heat into work by a machine operating between two temperatures.

If we place a body having the temperature, T_1, in thermal contact with a colder body having the temperature, T_2, we invariably find that heat flows from the hot body to the cold body and never in the reverse direction. That is, **heat energy will never of itself flow from a lower to a higher temperature but only in the reverse direction.** This result can be shown to be a necessary consequence of the laws of mechanics applied to a mechanical system composed of moving masses such as the molecules of a body and from the kinetic point of view is equivalent to the statement that, if a system composed of a large number of moving masses, such as the molecules of a perfect gas, having the average kinetic energy, $\frac{1}{2} mu_1^2$, is brought into contact with a second similar system having the average kinetic energy, $\frac{1}{2} mu_2^2$, in such a manner that a distribution of momentum and of kinetic energy can occur, the resultant transfer of kinetic energy will necessarily be in the direction of the system having initially the smaller value of $\frac{1}{2} mu^2$. Whenever, therefore, two bodies of matter at different temperatures are brought into thermal contact in any way there will occur a transfer of molecular kinetic energy (*i.e.*, a flow of heat) from the hotter to the colder body. In this flow of heat just as in the case of the moving electrons described above, we recognize once more, the transfer of a finite amount of *ordered* or *directed* kinetic energy in *one* direction and there exists, therefore, just as in the case of the electric current, the possibility of transforming this directed energy into some form of useful work.[2]

[2] The statement that heat will, of itself, flow only from a higher to a lower temperature and never in the reverse direction is one of the several methods of expressing the basic principle upon which the Second Law of Thermodynamics rests. This basic principle regarding the uni-directional autogenous, flow of heat is, moreover, usually regarded as essentially a new principle, that is, one which cannot be derived from the law of conservation of energy and the ordinary principles of mechanics. This view, however, becomes unnecessary if we accept the kinetic interpretation of the meaning of heat energy. That is, if we regard the heat energy of a material body or system as the energy which it possesses by virtue of the unordered motion of its atoms and molecules, then it follows from the ordinary principles of mechanics that the transfer of heat energy can only take place from a higher to a lower temperature. The criterion by which we determine which of two bodies or systems has the higher temperature then becomes the following: Let

This being the case, the question naturally arises as to how much *ordered* or *directed* kinetic energy is associated with the passage of a quantity of heat from a higher to a lower temperature, for it is this ordered energy only which is available for transformation into useful work.[3] In order to discover this it will only be necessary to carry out a couple of "imaginary experiments." Suppose we have two large heat reservoirs each of practically infinite heat capacity. Let the first reservoir have the temperature, T_1, and the second, the temperature, T_2, and let the two reservoirs be very close together but insulated from each other so that no transfer of heat from one to the other occurs. We will suppose, further, that in the interior of the first reservoir we have a quantity of some monatomic, perfect gas, such as helium under low pressure, for example.

Let the following imaginary experiments be carried out: (1) Place the two reservoirs in thermal contact for such a length of time that a finite quantity, Q_1, of heat passes from the first reservoir to the second. The passage of this heat may be assumed to take place either by radiation, or by conduction (along a metallic connecting rod, for example), or by any other mechanism whatsoever. After the passage of this quantity of heat the two reservoirs are again completely insulated from each other.

a quantity of a perfect gas be placed in thermal contact with the first system for a sufficient time for thermal equilibrium to establish itself. Call the average kinetic energy of the molecules of the gas under these conditions, $\frac{1}{2} mu_1^2$. Now take the gas and place it in thermal contact with the second system until thermal equilibrium is established. Its average molecular kinetic energy is now $\frac{1}{2} mu_2^2$. If $\frac{1}{2} mu_1^2 = \frac{1}{2} mu_2^2$, the two systems are said to have the same temperature. If the two kinetic energies are not equal then the system in which $\frac{1}{2} mu^2$ has the greater value is at the higher temperature.

[3] The amount of ordered kinetic energy involved in the transfer of a given quantity of heat, Q, from T_1 or T_2 is a definite characteristic of the quantity Q and the two temperatures T_1 and T_2 and is independent of the manner in which the transfer occurs. For, if this were not the case, that is, if the amount of ordered kinetic energy associated with the passage of Q calories of heat from T_1 to T_2 by one process of transfer were different from that by some other process of transfer, it can be readily proved that the two processes could be combined in such a way as to yield a result which would amount simply to an autogenous flow of heat from a lower to a higher temperature, a result which has been shown above to be impossible.

Now as far as the transfer of *energy* is concerned, the net result of the above experiment can be exactly duplicated by the following process: (2) Take from the first reservoir such a number, n, of molecules of helium gas that the total kinetic energy, $\frac{1}{2} nmu_1^2$, possessed by them shall be the exact equivalent of the quantity of heat, Q_1, which flowed from the first reservoir to the second, in the process just described. Transfer this quantity of gas bodily to the second reservoir and allow it to come into equilibrium with the reservoir keeping its volume constant. The gas will give up some of its energy to the second reservoir and will thus attain the temperature, T_2, of this reservoir, at which temperature its molecules will have the total kinetic energy, $\frac{1}{2} nmu_2^2$. If the gas be now returned to the first reservoir again, the whole system will be in the same condition as it was at the end of our first experiment.

It is clear that the net result of our second experiment consists simply in the transfer of the quantity of kinetic energy, $\frac{1}{2} nmu_1^2 - \frac{1}{2} nmu_2^2$, *in a definite direction;* that is, from the first to the second reservoir, from T_1 to T_2. This represents ordered or directed energy and is, therefore, available for conversion into useful work with the aid of some suitable mechanism whose nature we are not at present concerned with. Since, as explained in footnote 3 on the preceding page, the quantity of ordered or directed kinetic energy involved in the transfer of a given quantity, Q_1, of heat from T_1 to T_2 is independent of the way in which the transfer occurs, the relation

$$n(\tfrac{1}{2} mu_1^2 - \tfrac{1}{2} mu_2^2) = W \tag{5}$$

is a perfectly general expression for the available work of such a transfer. In this expression n represents that number of molecules of a monatomic perfect gas which at the temperature, T_1, have a total kinetic energy, $\frac{1}{2} nmu_1^2$, equivalent to Q_1 and which at the temperature T_2 have the total kinetic energy, $\frac{1}{2} nmu_2^2$.

8. Carnot's Equation.—Equation (5) really represents the essence of the Second Law of Thermodynamics. It is customary, however, to express the Second Law equation in terms of *quantity of heat and temperature* rather than in terms of molecular kinetic energy. Before translating equation (5) into these terms, however, we will first define the terms **engine, heat engine,** and **perfect engine.**

Any system or arrangement of matter which works in a cycle and converts any form of energy into some desired form of useful work will be called an **engine.** The expression, "working in a cycle," means that the working system periodically returns to its initial condition. An engine which works between two different temperatures and converts heat into work will be called a **heat engine.** In all real heat engines the efficiency is usually very low owing to losses caused by friction and by radiation and conduction, and owing also to the fact that in actual practice it is not energy which is desired so much as **power,** that is, energy per second. As a result we do not operate our engines in practice in such a way as to obtain the maximum amount of work which they are capable of yielding for that would mean that the rate of production of work would be exceedingly low. Instead, we sacrifice some of the possible work for the purpose of getting what we do obtain, at a higher speed.

We can, however, imagine an engine in which all the parts work so smoothly that there are no friction losses; in which heat insulation is so perfect that there are no energy losses due to radiation or conduction of heat; and which is operated so slowly that at every moment it is performing all the work it is capable of; that is, it acts always against an external force practically equal to the internal forces which are driving it. Such an imaginary engine will be called a **perfect engine.** It evidently represents a limiting condition approached by all real engines as the losses mentioned above are reduced to a minimum.

In the case of a perfect heat engine operating between the two temperatures, T_1 and T_2, in such a way that it takes up Q_1 calories of heat from a reservoir at the temperature, T_1, and transforms part of it into work, the question naturally arises as to what fraction of the Q_1 calories of heat such an engine is able to transform into work. This is the question which occurred to a young French engineer, Sadi Carnot,[a] about 1824, and his answer

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[a] Sadi Nicolas Leonhard Carnot (1796–1832). The eldest son of one of Napoleon's generals; a captain of Engineers in the French army. A young man of remarkably brilliant mind; a profound and original thinker; the founder of modern thermo-dynamics. His only published work, *Reflexions sur la puissance motrice der feu et sur les machines propres a developper cet puissance*, appeared in 1824 when he was 28 years of age. He died of the cholera in Paris at the age of 36.

to it constitutes one of the common forms of stating the Second Law of Thermodynamics.

In order to obtain Carnot's equation from our equation (5) we will first multiply and divide the left hand member by $\frac{1}{2}nmu_1^2$, and obtain

$$\frac{n(\frac{1}{2}mu_1^2-\frac{1}{2}mu_2^2)(\frac{1}{2}nmu_1^2)}{n(\frac{1}{2}mu_1^2)}=W \tag{6}$$

Now it will be recalled that $\frac{1}{2}nmu_1^2$ is the quantity of heat energy possessed by the n molecules of helium gas at the temperature T_1 and represents therefore the quantity of heat, Q_1, which was transferred from the first to the second reservoir (from T_1 to T_2), in the process described above. Equation (6) may, therefore, be written

$$\frac{(\frac{1}{2}mu_1^2-\frac{1}{2}mu_2^2)}{\frac{1}{2}mu_1^2}Q_1=W \tag{7}$$

and since according to equation (29, II), the mean kinetic energy of the molecules of a perfect gas is proportional to the absolute temperature of the gas, our equation becomes

$$\frac{\epsilon T_1-\epsilon T_2}{\epsilon T_1}Q_1=W \tag{8}$$

or

$$\frac{T_1-T_2}{T_1}Q_1=W \tag{9}$$

which represents Carnot's method of expressing what is now called the Second Law of Thermodynamics.

From our method of deriving this relation it is evident that the fraction $\frac{T_1-T_2}{T_1}$ is that part of the Q_1 units of heat which represents the amount of ordered or directed kinetic energy which is transferred from T_1 to T_2 and which is, therefore, available for performing useful work. Stated in other words, equation (9) signifies that any heat engine which operates between two temperatures, T_1 and T_2, in such a manner that it takes up Q_1 units of heat at the temperature, T_1, and converts part of it into work can never, even under the most favorable conditions imaginable (*i.e.*, those attained with a perfect heat engine), convert more than the fraction, $\frac{T_1-T_2}{T_1}$, of this heat into work, for this fraction, as we have just seen, represents the total amount of ordered kinetic energy which is involved in the passage of Q_1 units of heat from T_1 to T_2.

Only when T_2 equals zero would it be theoretically possible to convert all of the Q_1 units of heat into work. In other words, if surroundings at a temperature of absolute zero were available for our use, a perfect heat engine could convert into work all of the heat energy which it absorbed at any temperature. This, of course, merely means that in order to convert *all* of the molecular kinetic energy of any body into some form of useful work it would be necessary to bring *all* the molecules of the body to rest. Since we have no surroundings available at a temperature of absolute zero we have to content ourselves with slowing up the molecules of our working system as much as possible and to this end the temperature T_1 should always be made as low as feasible and the difference, $T_1 - T_2$, as large as feasible.

The most common form of heat engine employed in practice is the **steam engine.** The working system is water vapor enclosed in a cylinder provided with a movable piston and the heat energy is converted directly into mechanical work. The two temperatures between which the steam engine operates are the boiler temperature, T_1, and the temperature of the exhaust, T_2. The boiler temperature is usually maintained by the combustion of some kind of fuel. The temperature of the exhaust is not lower than the temperature of the surroundings.

In practice considerable quantities of heat energy escape from the boiler to the surroundings by radiation and conduction instead of being taken up by the engine and employed in doing useful work. Part of the work done by the engine is also converted back into heat again by the friction of the moving parts of the engine and is, therefore, not available. Moreover, as stated above, engines are not operated in practice so as to perform at all times the maximum work which they are capable of doing. As the result of all these losses the efficiency of steam engines employed in practice is much lower than that of a perfect heat engine. Thus, a perfect heat engine taking superheated steam at a temperature of 206.4° and delivering it to a water-cooled exhaust at a temperature of 43.1° would convert, $\frac{T_1 - T_2}{T_1} = \frac{206.4 - 43.1}{206.4 + 273.1}$

=34 per cent. of the heat energy of the steam into mechanical work. The most efficient 1000-H.P. steam engine which has ever been constructed,[4] when working under substantially the same conditions converts only 25 per cent. of the heat energy it receives into useful work, while for most steam engines as employed in practice this figure will average only about 8–10 per cent.

When figured on the basis of the total available energy obtainable from the coal, the efficiency is much smaller even. It can be shown that every gram of carbon which is burned to CO_2 should theoretically be capable of yielding about 34,000 joules of energy (at ordinary temperatures) in the form of useful work. This amount of carbon, if burned under conditions analogous to those under which coal is burned in the best modern boiler practice, will deliver to the engine about 27,000 joules of energy in the form of heat and 25 per cent. or 6800 joules of this would be converted into useful work by the 1000-H.P. engine mentioned above. That is, the most efficient modern engineering methods can obtain from coal only about, $\frac{6800}{34000}$ or 20 per cent. of its theoretical work producing power. The remaining 80 per cent. is lost.[5] Under average working conditions only 5–7 per cent. of the energy of the coal is obtained in the form of useful work. It is evident, therefore, that modern methods of converting the energy of coal into useful work are really exceedingly wasteful.

9. Free Energy and the Principle of the Degradation of Energy.—In addition to the energy which is obtainable from the chemical reaction, $C+O_2=CO_2$, which represents the combustion of carbon, many other chemical reactions are also capable of yielding

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[4] A Nordberg, air compressor, quadruple expansion engine with regenerative heating system. For the tests on this engine see Hood, Trans. Amer. Soc. Eng., 1907, p. 705.

[5] By employing mercury vapor instead of water vapor as the working medium, the efficiency of a vapor heat engine could be increased, because the boiling point of mercury (357°) is 257° higher than that of water and a higher initial temperature (T_1) could, therefore, be employed. Recent experiments by Emmet (Proc. Amer. Inst. Elec. Eng., **33**, 473 (1914)) indicate that a mercury vapor engine connected in tandem with a steam engine would show a 45 per cent. increase in efficiency (per lb. of fuel) over the steam engine alone. An experimental engine of this kind is under process of construction.

energy which can be made available for the production of work. In fact, in the case of every process whether chemical or physical, which tends to take place of itself, a portion of the total energy decrease, $-\Delta U$, which accompanies the process can always be obtained in the form of useful work, if the process is allowed to take place in a suitable manner. The maximum amount of work which the process is theoretically capable of yielding when carried out in such a way as to operate a perfect engine of some character is called the **"free energy,"** A, of the process. The free energy of a chemical reaction is an important and characteristic property of the reaction.

In order to make clearer the distinction between the free energy, A, of a reaction and its total energy, $-\Delta U$, we will consider the chemical reaction,

$$Zn + Hg_2SO_4 + 7H_2O = ZnSO_4 \cdot 7H_2O + 2Hg$$

which occurs when a rod of metallic zinc is placed in an aqueous solution saturated with mercurous sulphate. In this reaction the zinc dissolves and throws out the mercury. When allowed to occur in this way, there is evidently no work[6] done by this reaction and the total energy, $-\Delta U$, liberated by the reaction must appear entirely in the form of heat. That is, by the First Law (equation (1)) we have

$$-\Delta U = -Q = 81{,}320 \text{ cal. of heat evolved.}$$

If instead of allowing the reaction to proceed in the above way, we place the mercury in the bottom of a tube, cover it with a paste of mercurous sulphate and then fill the tube with a saturated solution of zinc sulphate in which the rod of zinc dips, we will find on connecting the zinc and the mercury to the terminals of a voltmeter that there exists a difference of potential between them amounting to 1.429 volts at 18° and if they be connected to the terminals of a perfect electric motor, a current of electricity (193,000 coulombs of electricity for each atomic weight of zinc dissolved) will pass through the motor during the time the above reaction is taking place, and this current can thus be made to do

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[6] With the exception of the very insignificant amount of work done against the pressure of the atmosphere owing to the fact that there is a slight change in volume in the above reaction.

useful work. The maximum amount of work which it is capable of doing represents the free energy of the reaction and is evidently given by the expression (X, 5)

$$A = E \times q = 1.429 \text{ volts} \times 193{,}000 \text{ coulombs} = 275{,}800 \text{ joules} = \frac{275800}{4.184} = 65{,}880 \text{ calories.}$$

The rest of the energy of the reaction appears in the form of heat and amounts to $-Q_2 = 15{,}440$ calories. We have, therefore,

$$-\Delta U = -Q + W = -Q_2 + A = 15{,}440 + 65.880 = 81{,}320 \text{ calories.}$$

Most of the processes which occur in nature and in the industries take place in such a way that the whole or the greater part of the energy which they give out appears entirely in the form of heat which is then radiated and conducted away to the surroundings and thus is no longer available for the production of work. This constant transformation of available energy in various forms into unavailable heat energy is called the degradation of energy and the Second Law of Thermodynamics is sometimes called the **Principle of the Degradation of Energy** because it points out that heat energy at the temperature of our surroundings is not available for transformation into useful work. The Principle of the Degradation of Energy is more comprehensive than the Second Law of Thermodynamics as embodied in the Carnot equation, however, for there are other ways in which the capacity of a system for doing work can diminish besides the mere conversion of a part or the whole of its available energy into heat. For example, when a gas is allowed to expand into a vacuum it does no work. Some of its work-producing power has been lost by the process, however, for it might have been made to lift a weight during its expansion. Many other examples of processes which are attended by a loss of work-producing power, that is, a loss of "free energy" as it is also called, might be cited and our experience teaches us that the available energy of our world is constantly decreasing owing to the continual occurrence of such processes in nature and in the industries. This statement is the Principle of the Degradation of Energy. According to the first principle of energy (Principle of Conservation) the *total energy* of the universe is a constant, but according to the second principle (Principle of Degradation) the *available* energy of the world is constantly decreasing.

The two laws of thermodynamics are of great importance in physical chemistry since they enable us to derive a large number of important relations governing equilibrium in physical and chemical systems under a variety of conditions. We shall have occasion to employ a number of these thermodynamic relationships in the following chapters but will postpone the derivations of most of them until later. In the next section an application of the Second Law to a system at constant temperature is described.

10. Proof of Equality of Vapor Pressures at the Freezing Point.—Consider a pure liquid at A (Fig. 15) in contact at bb′ with its solid crystals in B, the space above both the liquid and solid being filled with the vapor. Assume that both the liquid and solid are at the temperature of the freezing point and hence (by definition) in equilibrium with each other at bb′. If their vapor pressures are not equal then one of them must be greater than the other. Suppose the vapor pressure of the liquid is greater than that of the solid. If this be the case the liquid will evaporate at A and the vapor (which according to our supposition has too high a pressure to be in equilibrium with the solid) would condense to solid again at B, and this process of distillation would continue until all of the liquid had been converted into solid which would be contrary to our assumption that they were initially in equilibrium with each other. The only other possibility is that, as fast as the liquid is used up by evaporation at A, it is replaced by the melting of the solid at bb′. Under this arrangement we

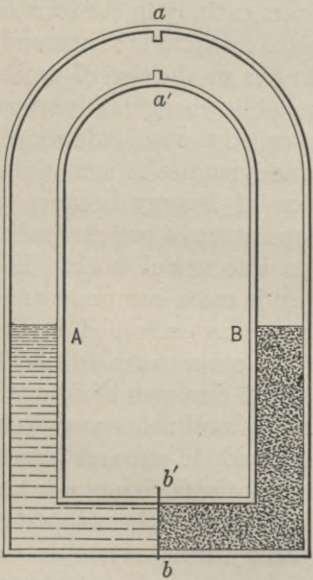

FIG. 15.

would have a constant stream of vapor passing by the position aa′ in the direction A→B and by placing a turbine at this point we could obtain work from a system working in a cycle at constant temperature which would be contrary to the Second Law of Thermodynamics (X, 7). Hence the vapor pressure of the liquid cannot be greater than that of the solid. In the same way it can be shown that the vapor pressure of the solid cannot be greater than that of the liquid. They must, therefore, be equal and the freezing point is, therefore, the point at which the vapor pressure curve of the liquid intersects that of the solid. (See Fig. 16.)

By a similar method of proof it can be shown that if any two phases are both in equilibrium with a third phase they are in equilibrium with each other.

11. Free Energy and the Carnot Equation.—Since in equation (9) W represents the maximum work obtainable from Q_1 units of heat by means of a perfect heat engine, it also represents the free energy of the process which occurs during the operation of the engine, Q_1 being the heat of the process (heat absorbed) at the temperature T_1. In equation (9) we may therefore write $W = A$ and, if we also put $T_2 = T$ and $T_1 = T + \mathrm{d}T$, we have

$$\mathrm{d}A = Q\frac{\mathrm{d}T}{T} \tag{10}$$

which is a convenient way of expressing the Second Law so as to show the manner in which the free energy of any process changes with the temperature at which the process occurs, the temperature being understood to remain constant while the process in question takes place. Q is similarly the heat *absorbed* during the occurrence of the process in a perfect engine at the temperature T. In order to integrate this equation and thus obtain an expression from which the free energy of any process (a chemical reaction, for example) can be computed at any temperature, it is first necessary to express Q as a function of T. Methods for doing this will be discussed in Chapter XX.

CHAPTER XI

SOLUTIONS I: DEFINITION OF TERMS AND CLASSIFICATION OF SOLUTIONS

1. Definition of a Solution.—In our first chapter (I, 2) we applied the term **mixture** to any material which is composed of more than one species of molecule. In this and the following chapters we shall deal with an important class of mixtures known as **solutions.** A solution may be defined as a one-phase system composed of two or more molecular species (see definition of phase, I, 8). The exact significance of this definition will be more easily understood from the following considerations.

If we grind together sugar, $C_{12}H_{22}O_{11}$, and sand, SiO_2, we can obtain an intimate mixture of these two materials, but on close examination we can readily recognize the presence of *two* crystalline phases, namely, crystals of pure sand and crystals of pure sugar, in the mixture. This mixture is, therefore, heterogeneous (I, 8) and is hence not a solution. Similarly, if we shake together (1) liquid mercury and liquid benzene, or (2) liquid mercury and gaseous nitrogen, or (3) liquid mercury and sugar crystals, we obtain in each instance systems in which the presence of *two* phases is readily recognized. Moreover, a chemical examination of the liquid and the crystalline phases in each of the above systems would fail to give any evidence of the presence of more than one molecular species within the phase, and without such evidence we could not class any one of the phases as a solution.

By bringing together (1) liquid water and liquid alcohol, or (2) liquid water and gaseous hydrochloric acid, or (3) liquid water and sugar crystals, however, we can obtain in each instance a *one-phase* (*i.e.*, *homogeneous*) system in which the presence of more than one molecular species can be readily ascertained. We obtain, therefore, in each of these cases a solution.

In a true solution,[1] after equilibrium is reached, the *individual molecules* of the different molecular species present are intimately and uniformly mixed with one another, or, in another phraseology which is frequently used, the different component substances which were brought together in order to prepare the solution have become **molecularly dispersed** in one another. The different molecular species of which a solution is composed will be called its **molecular components** and the substances corresponding to these molecular species, or more generally the substances of which the solution is considered to be composed, will be called its **components** or its **constituents.** For example, a solution whose **constituents** are the *pure* substance, sugar, and the *associated* substance, water, has the following **molecular components:** (H_2O), $(H_2O)_2$, $(H_2O)_3$, $C_{12}H_{22}O_{11}$, $C_{12}H_{22}O_{11}\cdot(H_2O)_x$, and possibly others.

2. Associated Substances as Solutions.—An associated substance (III, 5) such as water must, strictly speaking, be itself classed as a solution since it contains more than one species of molecule. It is a solution of a peculiar character, however, because the different molecular species all have the formula $(H_2O)_x$, where x is an integer, and these species are, moreover, all in chemical equilibrium (I, 9) with one another, the equilibrium being established so rapidly that we are unable to separate any one of the molecular species from the others. Chemically, therefore, and in many ways physically also, water behaves as it would if it contained only the molecular species, H_2O, and is for this reason commonly spoken of as a "pure substance." Regarded as a solution, water is considered to be made up of the substances hydrol, H_2O, dihydrol, $(H_2O)_2$, trihydrol, $(H_2O)_3$, etc., no one of which, however, has as yet been obtained in the pure condition, at least not as a liquid. Owing to the fact that in so many ways an equilibrium mixture, such as water, resem-

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[1] The term "true" solution is used here because of the existence of the class of systems to which the name "colloidal solutions" has been given. These systems consist of one phase *very highly* dispersed in another and occupy a position intermediate between homogeneous mixtures ("true" solutions) on the one hand and the ordinary heterogeneous systems on the other. They have already been discussed to some extent in Chapter IX and will be further considered in Chapter XXV.

bles a pure substance in its behavior, it is convenient to class such mixtures with pure substances for many purposes and for this reason the term *associated substance*, rather than the term solution, is usually applied to them. The expression "pure water" can, therefore, be employed, if we agree to understand thereby an equilibrium mixture of molecules all of which have the formula $(H_2O)_x$, where x is an integer, and in which the equilibrium responds so rapidly to changing conditions (temperature, pressure, etc.) that it may be regarded as establishing itself practically instantaneously[2] at each moment.

3. Classification of Solutions.—For purposes of systematic treatment solutions are most conveniently classified, according to their state of aggregation, as **gaseous solutions, liquid solutions,** and **crystalline solutions.**

(*a*) **Gaseous Solutions.**—Gaseous solutions furnish the simplest example of solutions, since the molecules are here so far apart that they are comparatively without influence upon one another. Owing to this fact many of the physical properties of mixtures of perfect gases are strictly additive (VIII, 3), that is, a molal physical property for a mixture of gases may be calculated by means of the relation,

$$y = y_A x_A + y_B x_B + \quad . \ . \ . \ . \quad y_N x_N \tag{1}$$

where y is the molal property in question (*e.g.*, molal volume, molal heat capacity, or molal (molecular) refractivity) for the mixture and y_A, y_B, etc., are the corresponding molal properties for the pure constituents of the mixture, x_A, x_B, etc., being their mole fractions in the mixture. Equation (1) is an expression of the so-called **law of mixtures.** It will be noticed that Dalton's law of partial pressures (II, 6) for gaseous mixtures has the same form as the above equation.

Problem 1.—Two tubes, 10 mm. in diameter, are placed side by side so that white light of a constant and uniform intensity illuminates them lengthwise. The first tube is 50 mm. long and is filled with iodine vapor

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[2] Numerous other liquids in which there exists a chemical equilibrium which responds very rapidly to changes in external conditions behave in many ways as though they were pure substances, and for many purposes may advantageously be classified as such. The numerous tautomeric substances familiar to the organic chemist are good examples of such systems.

(I_2) under a pressure of 0.06 atmosphere. The second tube is 500 mm. long and is filled with a gaseous mixture of hydrogen (H_2) and iodine (I_2) under a pressure of 0.06 atmosphere. Both tubes are at a temperature of 100° and when compared with each other are found to show the same shade and intensity of violet color when viewed lengthwise toward the source of white light. Calculate the concentration (in moles of I_2 per liter) of the iodine in the second tube.

Owing to the comparatively large distances between the molecules of gases and the consequent lack of influence of one molecule upon another, no energy change occurs when any two perfect gases are mixed together in the same volume, provided that they do not react chemically with each other. This is made evident by the absence of any temperature change when two such gases are mixed together. Similarly when a perfect gas is allowed to expand into a vacuum there is no change in its temperature. These statements do not hold for gases under high pressures, however, for here very pronounced energy changes (heat effects) occur when expansion or mixing takes place. We shall have occasion to consider such energy changes in a later chapter.

In the case of gaseous mixtures at such high pressures or at such low temperatures that the perfect gas laws do not apply with a sufficient degree of accuracy, modifications of these laws along lines similar to those followed by van der Waals or Berthelot in their treatment of pure gases (II, 10) are usually employed. We shall not consider them further in this book.

(*b*) **Crystalline Solutions.**—The subject of crystalline solutions, or mixed crystals, has been briefly referred to in a previous chapter (V, 4). Owing to the restricted nature of molecular motion in crystals and the high viscosity of this state of aggregation, crystalline solutions in a state of equilibrium are seldom met with in practice, because the attainment of equilibrium in a reasonable length of time is so frequently prevented by the restraints upon the free movements of the molecules. (Cf. V, 3.) For this reason crystalline solutions, as usually met with in practice, are not amenable to the same methods of treatment as are nearly all gaseous and liquid solutions. This same statement frequently holds true also, and for the same reason, for the glasses (VII, 3), which represent one type of liquid solutions. The discussion of such cases of crystalline solutions as may be treated as systems in thermodynamic equilibrium will be taken up in connection with the chapter on the Phase Rule (XXIV, 12).

(*c*) **Liquid Solutions.**—The most interesting group of solutions to the chemist is the class of liquid solutions, because by far the greater portion of the processes of the chemist are carried out in such solutions and because they play such a predominant and important rôle in natural processes. For these reasons liquid solutions have been and continue to be the subject of the most careful study, and the discovery of laws and the establishment of satisfactory theories for the interpretation of many of the processes occurring in such solutions has been one of the chief triumphs of modern physical chemistry. In the following chapters dealing with the subject of solutions we shall, therefore, restrict ourselves to the class of liquid solutions.

4. The Constituents of a Solution. Solvent and Solute.—When crystals of some substance, such as sugar, are treated with water, the crystals are observed to gradually dissolve or disappear and a homogeneous system consisting of sugar and water is eventually obtained. Such a solution is commonly spoken of as a *solution of sugar in water* and is by some chemists regarded as having been formed owing to some specific *solvent* or *dissolving action* exerted by the water upon the sugar. For this reason the water is commonly called the **solvent,** and the sugar, the **dissolved substance** or the **solute.** It would be quite as correct, however, to look upon the solution as a solution of *water in sugar* and, as a matter of fact, it could be prepared by dissolving water in liquid sugar, if it were desired to do so. The sugar might then be called the **solvent** and water the **dissolved substance** or the **solute.** Similarly, if a little water (either as a liquid, or in the form of ice or steam) is "dissolved" in alcohol, a solution of *water in alcohol* is obtained. Exactly the same solution might be prepared, however, by "dissolving" alcohol (either solid, liquid, or gaseous) in water. The nature of the solution thus obtained is entirely independent of the method of its preparation, and the designation of one constituent as the solvent and the other as the solute, on the above basis, is an entirely artificial and arbitrary, not to say confusing, distinction. A better and more general method of distinguishing the constituents of a solution is simply to refer to them as constituent A, constituent B, etc., and this is the method which will be usually employed in this book. The terms **solvent** and **solute** will be employed chiefly in the treatment of an important class of solutions known as "dilute solutions," that is, solutions in which the amount of one constituent is much greater than that of all the other constituents together. For such solutions the term **solvent** will be employed to designate the constituent which predominates in the solution, without however implying thereby that this constituent exercises any specific solvent power upon the others. The other constituents will be called the **solutes.** This method of designation is in accordance with common usage but its purely conventional character should not be forgotten.[3]

The following general treatment of the subject of solutions will for simplicity be restricted, in most cases, to solutions made up of only two constituents which will be designated either as A and B, or as solvent and solute, respectively. The relations and laws which we shall derive can, however, be readily extended to solutions containing any number of components. Moreover, since any substance A, in the liquid state, can be regarded as a limiting case of a solution of B in A in which the amount of B has become zero, pure liquids may be treated as special limiting cases under the subject of solutions and will be in certain cases included in our treatment of the subject.

5. Methods for Expressing the Composition of Solutions.— The composition of a solution is frequently given in terms of **percentages** (*i.e.*, grams in 100 grams of solution) of its various constituents. In what follows we shall, however, usually express the composition of the solution in terms of the **mole fractions** (II, 6) of its different components. Thus, if a solution is composed of N_A moles of A and N_B moles of B, the mole fraction of A will be $x_A = \frac{N_A}{N_A + N_B}$ and that of B will be $x_B = \frac{N_B}{N_A + N_B}$ (II, 6) and hence,

$$x_A + x_B = \text{unity} \tag{2}$$

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[3] The common expression, "Water is the universal solvent," means that a large number of substances are able to become molecularly dispersed in water and that water occurs in large quantities in nature. The ability of two substances to become molecularly dispersed in each other is a reciprocal relationship, not a one-sided property as the expression "solvent power" might be taken to indicate.

Problem 2.—Calculate the two mole fractions for each of the following solutions: 10 grams of water (H_2O) and 3 grams of alcohol (C_2H_5OH); 8 grams of benzene (C_6H_6) and 1 milligram of diphenyl ($C_{12}H_{10}$); a 10 per cent. solution of sugar ($C_{12}H_{22}O_{11}$) in water.

Similarly, if we wish to express the composition of the solution in terms of its molecular components rather than its constituents (XI, 1) the same system will be employed on the basis of **molecular fractions,** $x_A=\frac{n_A}{n_A+n_B}$, $x_B=\frac{n_B}{n_A+n_B}$, etc., where n_A, n_B, etc., represent the numbers of molecules of the molecular species A, B, etc., which are present in the solution. In many cases the mole fraction of a substance in a solution will be identical with the molecular fraction of the corresponding molecular species. This will of course always be the case when each substance in the solution has only one molecular species corresponding to it. Thus in a solution composed of benzene and toluene the mole fraction of the substance, benzene (molal weight $=78$), in the solution is identical with the molecular fraction of the molecular species, C_6H_6; but in a solution composed of water and alcohol the mole fraction of the substance, water (molal weight $=18$), will not be identical with the molecular fraction of the molecular species, H_2O, because there is in the solution more than one molecular species corresponding to the substance, water. **Mole fraction** and **molecular fraction** will both be represented by the same symbol, x, and whenever it is necessary to distinguish between them this will be done in the context.

A common method of expressing the composition, especially of dilute solutions, is in terms of **concentration.** By the concentration, C, of any substance in a solution is meant the quantity of the substance per unit volume of solution. This may be expressed either as (1) moles, (2) formula weights, or (3) equivalent weights of the substance per liter of solution (I, 7). The terms (1) *molal*, (2) *formal*, and (3) *normal*, are used correspondingly to indicate the strength of the solution. Thus a solution containing 20.829 grams (*i.e.*, 0.1 of $(137.37+2\times35.46)$) of barium chloride, $BaCl_2$, per liter is said to be 0.1 *molal*, 0.1 *formal*, and 0.2 *equivalent* or 0.2 *normal* with respect to barium chloride. Sometimes 1000 *grams of solvent* is made the basis for expressing the concentration of the solution instead of 1000 *c.c. of solution.* Concentrations expressed on this basis are termed **weight concen-**

trations to distinguish them from the **volume concentrations** defined above. For the same reason the terms *weight-molal, weight-formal,* and *weight-normal* are correspondingly employed. Weight concentrations can be readily calculated from volume concentrations or *vice versa,* if the density of the solution is known.

Problem 3.—A solution of density, D, is $1/n$-weight formal with respect to a substance whose formula weight is M. What is its volume concentration in formula weights per liter?

Problem 4.—Calculate the weight-formal concentration of the first-named substance in each of the solutions given in problem 2. The last-named solution has at 20° a density of 1.038143 grams per cubic centimeter. What is its volume-formal concentration?

Problem 5.—Calculate the molal concentration of alcohol (C_2H_5OH) in a 5 per cent. solution of it in water. The density of the solution at 20° is 0.98936. Calculate also its weight-molal concentration and the mole fraction of the water (H_2O) in the solution.

Problem 6.—A 0.25 formal aqueous solution of H_2SO_4 has at 15° a density of 1.016. What per cent. of sulphuric acid does it contain? What is its volume normality with respect to sulphuric acid?

6. Vapor Pressure.—The vapor pressure, p, of a solution is equal to the sum of the partial vapor pressure of its constituents, or

$$p = p_A + p_B + \cdots \qquad (3)$$

7. Boiling Point.—The boiling point of a solution is defined as the temperature at which the vapor pressure of the solution is equal to the total pressure upon it. (Cf. IV, 3.)

8. Freezing Point.—A solution has in general as many freezing points as there are substances in the solution which are able to separate out as pure crystals. The freezing point of a given solution is the temperature at which the solution is in equilibrium with the pure crystals of one of its constituents. (Cf. VII, 1.) The nature of the crystalline phase must, therefore, always be stated except in the case of dilute solutions, where by general agreement, unless otherwise specified, the freezing point is understood to be the temperature at which the solution is in equilibrium with pure crystals of the constituent which is designated as the *solvent.*

CHAPTER XII

SOLUTIONS II: THE COLLIGATIVE PROPERTIES OF SOLUTIONS AND THE THERMODYNAMIC RELATIONS WHICH CONNECT THEM

1. Vapor Pressure and Temperature.—We have already noted (IV, 3) that the vapor pressure of a substance always increases with rise in temperature. In the case of any pure liquid or of any constituent of a solution under a constant external pressure, P (that of the atmosphere, for example), the rate of increase of the vapor pressure with rise in temperature is indicated mathematically by the partial differential coefficient, $\left(\frac{\partial p}{\partial T}\right)_{P,x}$. The subscripts (in this case P and x) indicate variables which are constant for the process under consideration. The above mathematical expression stated in words would be read as follows: the temperature rate of change of the vapor pressure of a pure substance (or of the partial vapor pressure of any constituent of a solution in which the mole fraction of the constituent is x) under constant external pressure, P; or more briefly, the partial of p with respect to T, P and x constant.

It can be shown that the Second Law of Thermodynamics leads to the following exact expression for this differential coefficient:

$$\left(\frac{\partial p}{\partial T}\right)_{P,x}=\frac{L_v}{v_0T} \tag{1}$$

where L_v is the molal heat of vaporization (IV, 2) of the substance and v_0 its molal volume in the vapor state under the conditions indicated.

For a pure crystalline solid we have, similarly,

$$\left(\frac{\partial p}{\partial T}\right)_{P}=\frac{L_s}{v_0T} \tag{1a}$$

L_s being the molal heat of sublimation (VI, 3).

If the substance is under its own vapor pressure at all temperatures, instead of under a constant external pressure, equations (1) and (1a) have the form

$$\left(\frac{\partial p}{\partial T}\right)_{x,P=p} = \frac{L}{(v_0 - V_0)T} \tag{2}$$

where V_0 is the molal volume of the liquid (or crystals) at the pressure P and temperature T. This is known as the Clausius[a]-Clapeyron[b] equation. Except in the neighborhood of the critical point, V_0 is usually so small in comparison with v_0 that it may be neglected and then equation (2) takes the form of equation (1), that is, equation (1), which is rigorously exact if P is constant, is also approximately correct for many cases where $P = p$.

Problem 1.—In order to integrate equation (1) or (1a) it is first necessary to express L and v_0 as functions of one of the variables. If the vapor obeys the perfect gas law and if L is a constant with respect to variations in T, show that the integral of the above equations has the form,

$$\log_e \frac{p_1}{p_2} = \frac{L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3}$$

Problem 2.—At −2° water has a vapor pressure of 3.952 mm. of Hg. Its heat of vaporization at 0° is 2495 joules per gram. Calculate its vapor pressure at 2°.

2. Variation of Boiling Point with External Pressure on the Liquid.

—Since by definition (XI, 7) vapor pressure, p, and external pressure, P, for any liquid are equal to each other at the boiling point, T_B, of the liquid, it follows that at this temperature

$$\left(\frac{\partial T_B}{\partial P}\right)_x = \left(\frac{\partial T_B}{\partial p}\right)_x \tag{4}$$

and hence from equation (2) above we find

$$\left(\frac{\partial T_B}{\partial P}\right)_x = \frac{(v_0 - V_0)T_B}{L_v} \tag{5}$$

or

$$\frac{1}{T_B}\left(\frac{\partial T_B}{\partial P}\right)_x = \frac{v_0}{L_v} \text{ (approx.)} \tag{6}$$

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[a] Rudolph Julius Emmanuel Clausius (1828–1888). Professor of Physics in the University of Zurich, the University of Würtzburg and until his death in the University of Bonn. One of the founders of modern thermodynamics.

[b] Benoit-Paul Emile Clapeyron, (1799–1864). French engineer and professor at L'École de Ponts et Chausseès.

Problem 3.—Compare the purely thermodynamic relationship expressed by equation (6) with the Crafts' equation, $\frac{1}{T_{B_0}}\frac{dT}{dP}=\text{const.}$ (IV, 5). What can you state with regard to the ratio, $\frac{L_v}{v_0}$ for pure liquids at their boiling points? Compare also with Trouton's rule, and draw a conclusion with regard to the ratio $\frac{v_0}{T_{B_0}}$ for related liquids.

3. Effect of Pressure upon Vapor Pressure.—If the pressure upon any pure substance in the liquid (or crystalline) state be increased, the vapor pressure of the substance also increases, the quantitative thermodynamic relation between the two being expressed by the equation,

$$\left(\frac{\partial p}{\partial P}\right)_T = \frac{V_0}{v_0} \tag{7}$$

where V_0 is the molal volume of the substance in the liquid (or crystalline) state at the pressure, P, and temperature, T. An equation of the same form,

$$\left(\frac{\partial p_A}{\partial P}\right)_{T,x} = \frac{\overline{V}_{0A}}{v_{0A}} \tag{8}$$

also holds for the effect of pressure upon the partial vapor pressure, p_A, of any constituent of a solution. $\overline{V}_{0A}$, the partial molal volume of A in the mixture, is equal to the increase in the volume of an infinite amount of the solution, which takes place when one mole of the substance, A, is added to it.

4. Vapor Pressure Lowering.—If to any pure liquid, A, having the vapor pressure, p_0, we add some substance which forms a solution with it, it can be shown both from molecular kinetics and from the Second Law of Thermodynamics that the vapor pressure of A is thereby lowered. In other words, the partial vapor pressure of any substance from a solution is always lower than its vapor pressure in the pure state. The **vapor pressure lowering,** Δp, is defined by the equation,

$$\Delta p = p_0 - p \tag{9}$$

and a quantity called the **relative vapor pressure lowering** is defined as $\frac{p_0-p}{p_0}$ or $\frac{\Delta p}{p_0}$ where p_0 is the vapor pressure of the substance as a pure liquid and p its partial vapor pressure from the solution, both being at the same temperature, T, and under the same external pressure, P.

5. Elevation of the Boiling Point.—**Problem 4.**—From what has just been said regarding the lowering of vapor pressure which occurs when one substance is dissolved in another, show that the following statement must also be true: The boiling point of a liquid is always raised by dissolving in it any substance whose own vapor pressure is negligibly small.

The **elevation of the boiling point,** or the **boiling point raising** as it is also called, is defined by the equation,

$$\Delta T_B = T_B - T_{B_0} \tag{10}$$

where T_B is the boiling point of the solution and T_{B_0} that of the pure liquid, both boiling points being of course for the same pressure. If the other constituent of the solution has an appreciable vapor pressure of its own, the boiling point is not necessarily raised when the solution is formed but may even be lowered, if the other constituent is a very volatile substance. This occurs, for example, when ether is dissolved in alcohol.

6. Freezing Point Lowering.—We have already seen (X, 10) that at the freezing point of a pure liquid the liquid has the same vapor pressure as the crystals with which it is in equilibrium. If to such a system a second substance is added which dissolves in the liquid, but not in the crystals, the vapor pressure of the liquid is thereby lowered and it will no longer be in equilibrium with the crystalline phase. The crystals, since they now have the higher vapor pressure, will tend to pass over into the solution which, if the two are in contact, they can do simply by melting. The process of melting is, however, attended by an absorption of heat (VII, 2), and consequently the whole system will cool down until some temperature is reached where the vapor pressure of the substance in the crystalline state is again the same as its partial vapor pressure from the solution and hence the two phases become once more in equilibrium with each other. That such a temperature will be reached can be demonstrated thermodynamically and can also be seen from a study of Fig. 16. This temperature we have already defined (XI, 8) as the freezing point of the solution and the freezing point of a liquid is, therefore evidently always lowered by dissolving another substance in it. The **freezing point lowering** is defined by the equation,

$$\Delta T_F = T_{F_0} - T_F \tag{11}$$

where T_{F_0} is the freezing point of the pure liquid and T_F that of the solution.

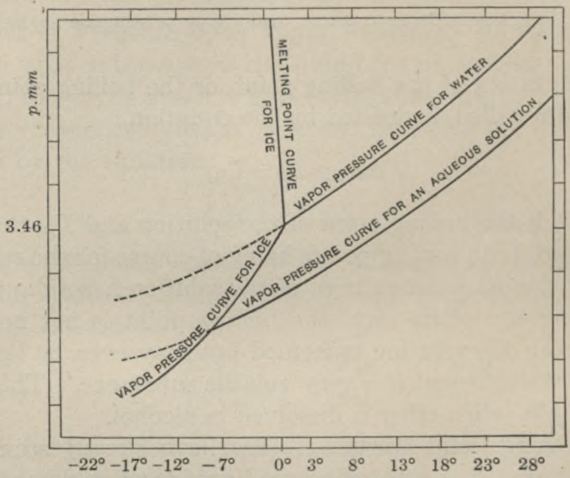

Fig. 16.

7. Osmotic Pressure and Osmosis.—Consider two vessels placed side by side under a bell-jar as shown in Fig. 17. Let vessel number 1 contain any solution, made up of any number of constituents, A, B, C, etc., and let vessel number 2 contain any one of these constituents, A for example, in the form of a pure liquid.[1] The partial vapor pressure of A from the first vessel is less than its vapor pressure from the second vessel (XII, 4) and hence there will be a tendency for the substance, A, to pass over from the pure liquid state (vessel 2) into the solution (vessel

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[1] In the most general case vessel number 2 might contain constituent A, dissolved in some other pure liquid to form a solution of any stipulated strength. This other pure liquid would, in such a case, serve simply as a *standard reference liquid* and for theoretical purposes might be some wholly hypothetical liquid, endowed with any desired properties. Unless a *standard reference liquid* of some kind is specified, however, the constituent in question is usually considered as present in the pure liquid state in the second vessel.

1) which it might do by distillation, for example. Now as explained above (XII, 1) the vapor pressure of A from the two vessels could be made the same either by raising the temperature of the solution or by lowering that of the pure liquid, the total pressure on both remaining the same. Or, the two vapor pressures might also be made the same by keeping the temperature of both vessels constant but varying the total pressure on one of them, *i.e.*, by *increasing* the total pressure on the solution or by *decreasing* the total pressure on the pure liquid (XII, 3).

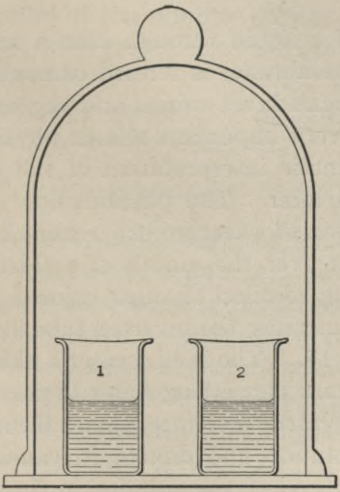

Fig. 17.

The difference in the total pressure upon the two vessels which is just sufficient to produce equality in the vapor pressures of A from both vessels is called the **osmotic pressure** of the solution with reference to constituent A and will be indicated by the symbol, Π_A. In order to completely define this pressure difference, the actual pressures on the two vessels must also be specified. Unless otherwise stated, therefore, we shall define the **osmotic pressure,** Π_A, by the equation,

$$\Pi_A = P - P_A \qquad (12)$$

where P_A is the pressure on the pure liquid, A, and P that on the solution, when A has the same vapor pressure[2] from both, and unless otherwise specified P will always be understood to be one atmosphere.

Problem 5.—Show by a method of reasoning similar to that employed in X, 10, that if a pure liquid, A, be separated from a solution containing it by a membrane which is *permeable only to molecules of* A, then A will pass through the membrane into the solution, if the solution and the pure liquid are both at the same temperature and pressure; but that if the pressure difference Π_A (as just defined) be established on the two liquids, then there will no longer be any tendency for A to pass through the membrane into the solution.

The passage of a liquid through such a membrane (called a **semipermeable membrane**) is termed **osmosis.** Semipermeable membranes are found in all animal and vegetable organisms and **osmosis** plays a very important rôle in physiological processes. The molecular kinetic interpretation of the process of osmosis will be discussed later. The phenomenon of osmosis can be easily demonstrated as a lecture experiment by tying a piece of gold beater's skin over the mouth of a thistle tube, filling the tube with a strong solution of sugar colored with a little cochineal and then immersing the inverted tube in a beaker of water, as shown in Fig. 18. The gold beater's skin acts as a semipermeable membrane permitting water to pass through it readily but not sugar. Water, therefore, passes through the membrane into the sugar solution and dilutes it, causing the volume to increase and the level of the solution in the tube to rise. The weight of the column of solution above the membrane and hence,

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[2] More generally stated the definition of Π_A would be $\Pi_A = P - P_A$, where P_A is the pressure on the pure liquid, A, and P that on the solution when A has the same *escaping tendency* from both. The vapor pressure of the molecules of the substance, A, from any phase or system containing it is only one of the many ways in which this escaping tendency may manifest itself. It is one which is very readily visualized by the student, however, and for that reason we shall employ it frequently. Increase of pressure upon a liquid not only increases its vapor pressure, that is, its tendency to escape into the vapor phase, but it also increases its tendency to escape into any other condition whatsoever, as can be readily shown by purely thermodynamic reasoning. While, therefore, the concept of escaping tendency in general is a more abstract method of expression, we shall for the present employ instead the more concrete concept of its manifestation as a vapor pressure.

therefore, the pressure upon the layer of solution next the membrane gradually increases and with a properly prepared membrane osmosis will continue until the resulting pressure becomes so great that the tendency of the water to pass through the membrane into the solution is just equal to its tendency to pass in the opposite direction, and consequently the rates of osmosis in the two directions balance each other and the column of liquid in the thistle tube ceases to rise. When this condition is reached the weight of liquid above the semipermeable membrane is a measure of the osmotic pressure of the sugar solution, with reference to the constituent, water.

This particular osmotic pressure, Π'_A, however, is obviously defined by the equation,

$$\Pi' = P - P_A = (P - 1) \text{ atmos.} \qquad (13)$$

where P is the pressure upon the layer of solution next to the semipermeable membrane. It is the osmotic pressure as defined by equation (13) rather than that defined by equation (12) which is usually obtained in *direct* osmotic pressure measurements. That is, it is the pressure difference necessary to establish equilibrium when the pure liquid (instead of the solution) is under atmospheric pressure. Either osmotic pressure Π_A or Π'_A may, however, be thermodynamically calculated, if the other is known, and in the case of aqueous sugar solutions of moderate concentrations the two osmotic pressures are practically identical. The one defined by equation (12) is, however, in general a simpler one to employ than is the one defined by equation (13).

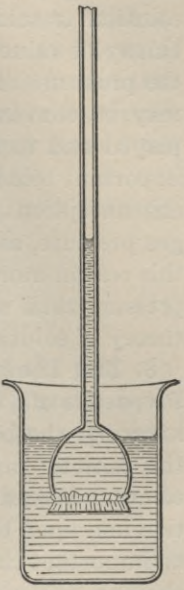

FIG. 18.

In direct osmotic pressure measurements with aqueous solutions the membrane employed is usually a film of cupric ferrocyanide deposited in the pores of a porous earthern cup. Direct measurements of osmotic pressure are difficult to carry out, however, and have thus far been accurately made only in the case of a few aqueous solutions. The osmotic pressure of any solution can be calculated thermodynamically, however, from the freezing point or from the vapor pressure of the solution and this is, in the majority of cases, the most reliable as well as the most convenient method to employ in case one desires to know the osmotic pressure of any solution. The rôle played by osmotic pressure in the theory of solutions is of such a nature, however, that the knowledge of the numerical value of the osmotic pressure of any solution is seldom of much importance. Osmotic pressure is chiefly of value simply as a concept by means of which some of the processes employed in the derivations of the laws of solution may be conveniently visualized. Historically, however, it has played and to many chemists of the present day still plays an important rôle in solution theory, chiefly owing to some popular misconceptions as to its nature and the analogy between it and gas pressure, as will be explained further in Chapter XIV. For this reason more space will be given to the discussion of osmotic pressure than would be justified by its actual importance in the theory of solutions.

8. The Thermodynamic Relations Connecting the Colligative Properties of a Solution.—The magnitudes of the vapor pressure lowering, the boiling point raising, the freezing point lowering, the osmotic pressure, and certain other allied properties of a solution depend *in general* upon the molal composition of the solution and upon the natures of its constituents. But in the case of an important class of solutions which will be discussed in the next chapter, the magnitude of these quantities for one constituent of the solution depends only upon the nature of this constituent and upon its mole fraction in the solution and not at all upon the natures of the other components of the solution nor the relative amounts of them present.

Now although, *in general*, the magnitude of any one of these quantities depends both upon the composition of the solution and the natures of its constituents, the relation between any two properties for any constituent of any given solution depends only upon the nature of this constituent and not at all upon the mole fraction of the constituent in the solution nor upon the number or natures of the other constituents of the solution. Thus, for example, the relation connecting the partial vapor pressure of any constituent, A, of a solution with its osmotic pressure does not depend in any way upon the per cent. of A in the solution nor upon the number, amounts, or natures of the other substances in the solution. For these reasons the properties mentioned are called the colligative properties of the solution.

The exact and general relations which connect the colligative properties of a solution with one another can be easily derived[3] from the First and Second Laws of Thermodynamics without any additional assumptions. Relations of this character, that is, relations which are necessary consequences of the two laws of energy alone, will be referred to as "purely thermodynamic relations." We shall not stop here to explain further the details of the derivations of these relations but will simply state a few of them, using the nomenclature already employed.

(*a*) Vapor pressure, p, and freezing point, T_F, both with reference to the same constituent, A:

$$\left(\frac{\partial p_A}{\partial T_F}\right)_P = \frac{L_s}{v_0 T_F} \tag{14}$$

where L_s is the molal heat of sublimation (VI, 3) of the pure constituent at the pressure P, and the temperature T_F, and v_0 is the molal volume of its vapor at the pressure p_A, and the temperature, T_F.

(*b*) Vapor pressure and osmotic pressure for constituent, A.

$$\left(\frac{\partial p_A}{\partial \Pi_A}\right)_T = -\frac{V_0}{v_0} \tag{15}$$

V_0 being the molal volume of A in the liquid state at the temperature T, and the pressure $1-\Pi_A$, and v_0 the molal volume of the vapor at the pressure p, and the temperature T.

(*c*) Vapor pressure and boiling point, T_B: Since in this case by definition (XI, 7) $p=P$, the relation is simply equation (1) above, which may be written:

$$\left(\frac{\partial p}{\partial T_B}\right) = \frac{L_v}{v_0 T_B} \tag{16}$$

(*d*) Osmotic pressure and freezing point, both with reference to the same constituent, A:

$$\left(\frac{\partial \Pi_A}{\partial T_F}\right) = \frac{-L_F}{V_{0_A} T_F} \tag{17}$$

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[3] See Jour. Amer. Chem. Soc., **32,** 496 and 1636 (1910).

To these relations might be added many others, but the statement of additional ones will be deferred until they are needed. It will be noticed that none of the above equations contains any quantity which is in any way dependent upon the amount of the substance, A, present in the solution or upon the number, nature, or amounts of the other constituents of the solution.

There is, however, for every solution, a set of relations which connects each of the colligative properties of the solution with the nature of its constituents and its molal composition. This set of relations we shall call the "Laws of the Solution.". It is evident, from what has just been said, that in order to deduce the complete set of these laws for any given solution, it is necessary to have only one of the laws as a starting point, for all of the others can then be obtained by combining this one law with the purely thermodynamic relations discussed above. As our starting point in deducing the Laws of Solutions we shall employ the law connecting the partial vapor pressure of any constituent of a solution with its mole fraction in the solution.

Problem 6.—If the vapor is a perfect gas and V_0 is independent of π, show that the integral of equation (15) is

$$\Pi = \frac{-RT}{V_0} \log_e \frac{p}{p_0} \tag{18}$$

where p_0 is the vapor pressure of pure liquid A at the temperature T. Show also that this integral may be written in the form,

$$\Pi = \frac{RT}{V_0}\left[\left(\frac{p_0 - p}{p_0}\right) + \frac{1}{2}\left(\frac{p_0 - p}{p_0}\right)^2 + \frac{1}{3}\left(\frac{p_0 - p}{p_0}\right)^3 + \ . \ . \ . \ \right] \tag{19}$$

See Ref. 3 for the integrations of equations (14) to (17).

9. The Fundamental Vapor Pressure Law.—If in a solution having the two molecular components, A and B, the molecular fraction of A be increased from x_A to $x_A + dx_A$, the corresponding increase, dp_A, in its partial vapor pressure, p_A, is given by the expression,

$$dp_A = f_A(T.E.)dx_A \tag{20}$$

and similarly for component B,

$$dp_B = f_B(T.E.)dx_B \tag{21}$$

the temperature and total pressure being constant; or stated in words, when the molecular fraction of any component of a solution is increased by a very small amount, dx, the corresponding increase, dp, in its partial vapor pressure above the solution is equal to dx multiplied by a quantity which is a function of the thermodynamic environment (see XIII, 1) which prevails in the interior of the solution. It is evident that in order to integrate equation (20) it is first necessary to know the form of the function, $f_A(T.E.)$. The form of this function and the values of its parameters will in general be determined by the number, nature and relative proportions of the different constituents of the solution, and since in general these may be of the most varied character it is not practicable to attempt an evaluation of $f_A\ (T.E.)$ which will hold for all possible types of solutions. A better procedure is to classify solutions, as far as possible, with reference to this point, and then to seek an evaluation of $f_A\ (T.E.)$ for each class.

As our knowledge of solutions has progressed we have come to recognize two large groups or classes of solutions for which it is possible to evaluate this function in a satisfactory manner, or in other words, for which it is possible to construct more or less complete and satisfactory systems of laws and theories. These two classes may be called, respectively, (1) Solutions of Constant Thermodynamic Environment and (2) Solutions whose Thermodynamic Environment is a Function of the Ion-concentration. We shall restrict our consideration of the Theories of Solution to these two classes and in building up the system of laws for each class we shall follow the logical rather than the historical method of development, as our main purpose will be to present as clear and complete a picture as possible of the present condition of our systematized knowledge of solutions rather than to trace the stages by which this condition has been reached.

CHAPTER XIII

SOLUTIONS III: THERMODYNAMIC ENVIRONMENT. IDEAL SOLUTIONS AND DILUTE SOLUTIONS

1. Thermodynamic Environment.—Consider the two liquids, mercury, Hg, and benzene, C_6H_6, two substances which in their chemical and physical properties are widely different from each other. If we shake these two liquids together in a test-tube we find that neither substance will dissolve in the other to an appreciable extent. Instead, we obtain two liquid layers, one of which is practically pure mercury and the other practically pure benzene. The two species of molecules, Hg and C_6H_6, have scarcely any attraction for each other and refuse to intermingle. In other words, the substance mercury is not capable of existing in a molecularly dispersed state (XI, 1) under the conditions which prevail in liquid benzene, nor, on the other hand, are benzene molecules able to exist in the molecularly dispersed state in surroundings containing mercury molecules. This inability of these two liquids to mix with each other is closely connected with the great chemical and physical differences between them.

Suppose now that we replace the mercury by water [$H_2O + (H_2O)_2 + (H_2O)_3 + \ldots$], a liquid whose molecules resemble those of benzene more closely than mercury molecules do, and consequently (I, 2) one which in its physical and chemical properties is more like benzene than mercury is. On shaking water and benzene together we obtain, just as before, two liquid layers, a water layer below and a benzene layer above. On careful examination, however, we would find that the water layer contains a little benzene (about 0.1 per cent.) dissolved in it and that the benzene layer contains a little water (about 0.03 per cent.) dissolved in it. These two liquids are able, therefore, to mix with each other to a very slight but quite appreciable extent. In other words, an appreciable quantity of water is capable of existing in the molecularly dispersed state in an environment which is made up almost entirely of benzene molecules and similarly an appreciable quantity of benzene is able to exist in the molecularly dispersed condition in an environment made up almost entirely of water molecules.

Let us now take a third liquid, ethyl alcohol, which resembles benzene even more closely than does water. If we shake benzene, C_6H_6, and alcohol, C_2H_6O, together we find that we always obtain a homogeneous system whatever be the relative amounts of benzene and of alcohol taken, that is, these two liquids are miscible with each other *in all proportions.* The attractive forces of alcohol molecule for alcohol molecule, benzene molecule for benzene molecule, and alcohol molecule for benzene molecule are so related that when we pour alcohol into benzene the alcohol molecules intermingle with those of benzene and continue to do so in whatever numbers they are added. The first molecules of alcohol which enter the benzene find themselves surrounded by benzene molecules only. As the amount of alcohol is increased the *nature of the medium* surrounding any given alcohol or benzene molecule changes gradually from one composed almost entirely of benzene molecules to one in which the proportion of alcohol molecules gradually increases until finally the medium surrounding any given alcohol molecule or benzene molecule is composed almost entirely of alcohol molecules.

Now the tendency of a given molecule to escape from a solution containing it depends upon the conditions which prevail within that particular solution. The molecule is subject to the action of various attractive and repulsive forces as well as to collisions from the molecules which surround it and the sum total of all these environmental influences determines the magnitude of the escaping tendency of the molecule in question. An attempt to analyze further the nature of these environmental influences would in the present state of our knowledge be largely speculative and would have no particular value. It is, however, important to recognize the existence of these influences and their general character, and it will be convenient to have a name to designate the sum total of these effects. The *nature of the medium* surrounding any given molecular species in a solution will, therefore, be called the **thermodynamic environment** of this molecular species. The thermodynamic environment which prevails within a solution depends, in general, upon the relative numbers and the kinds of molecules which make up the solution and upon the temperature and the pressure.[1]

When the two molecular species which make up the solution are very different in character the thermodynamic environment prevailing within the solution will be so different from that which prevails within one of the two pure liquids, that a separation into two liquid layers will occur when the proportions of the two constituents reach certain values which are determined by the nature of the constituents and by the temperature and the pressure. Thus when we add water to benzene the water molecules intermingle at first with those of the benzene, forming a solution which has a thermodynamic environment practically the same as that which prevails in pure benzene. When the concentration of the water molecules reaches a certain value, however (which depends upon the temperature and the pressure), any further molecules of water added will not go into solution, since for concentrations higher than this value the mutual attractions of water molecule for water molecule become so great that any excess of water separates out as a new liquid layer, having a decidedly different thermodynamic environment.

In the case of alcohol and benzene which mix with each other in all proportions the two molecular species display many differences in both physical and chemical properties and the thermodynamic environments in the two pure liquids are probably quite appreciably different from each other, so that when alcohol is poured into benzene, the thermodynamic environment in the solution changes gradually from that which prevails in pure benzene to that which prevails in pure alcohol, but the total change in this instance is not so great but that both species of molecules are able to adapt themselves to it and hence do not find it necessary to form two distinct liquid layers possessing different thermodynamic environments.

To recapitulate, therefore, if molecules of a liquid, A, be introduced into a pure liquid, B, they intermingle with those of

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[1] And in some special cases, which will not be considered here, upon the amount and kind of light with which the solution is illuminated and upon the magnetic and electric condition of its surroundings.

B, forming a solution. As the concentration of the A molecules increases, two tendencies become manifest. First, the mutual attractions among the A molecules increase owing to the fact that these molecules are getting closer together as their concentration increases and as a result of this greater attraction there is a tendency for these molecules to collect together and to form themselves (together with some B molecules) into a second liquid layer having a different thermodynamic environment from the solution.

Opposed to this tendency toward separation and formation of a new thermodynamic environment is the fact that the increasing numbers of A molecules by their very presence in the solution are changing the thermodynamic environment of the solution and are making it more like that which would exist in the layer which tends to be formed by the mutual attractions of the A molecules. This naturally results in lessening the tendency of the A molecules to separate and form a second phase. When the two molecular species are greatly different from each other the first of these tendencies is likely to prove the stronger and two liquid layers are formed. The more nearly the two species of molecules resemble each other the greater will be the second tendency and when they are sufficiently alike the second tendency will predominate and the two substances will mix in all proportions.

Unless the two molecular species resemble each other *very closely*, however, the process of mixing is accompanied by quite an appreciable variation in thermodynamic environment in passing from one pure liquid through the series of mixtures to the other pure liquid, and although the two molecular species may be able to adapt themselves to the new thermodynamic environment and remain in solution together, this adaptation will in general be accompanied by external evidences in the way of heat effects (evolution or absorption of heat) and volume changes (expansion or contraction) which take place when the two liquids are mixed together. The magnitudes of these effects may be taken as a rough indication of the extent of the change in thermodynamic environment, in all cases where the process of mixing consists simply in the intermingling of the two molecular species and is not accompanied by chemical reactions. Thus when one mole of benzene is poured into a very large quantity of alcohol the change in thermodynamic environment undergone by the benzene molecules is accompanied by an absorption of 0.36 calorie of heat and by an appreciable change in volume, which indicates an appreciable but not very large change in thermodynamic environment. When one mole of alcohol is poured into a large quantity of benzene the process is accompanied by an absorption of 4 calories of heat. In this case, however, we have a chemical reaction, namely, $(C_2H_5OH)_x = xC_2H_5OH$, accompanying the process of mixing, for ethyl alcohol is an associated liquid (III, 5) and when it is poured into a sufficiently large quantity of benzene the associated molecules must (as we shall learn later) dissociate into simple ones and this reaction will be attended by a heat effect which will be added to that due to the change in thermodynamic environment alone. The total heat effect in such a case will not, therefore, be a trustworthy indication of the extent of the change in thermodynamic environment.

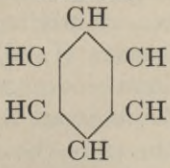
A better measure of the magnitude of this change is furnished by the decrease in free energy (X, 9) which accompanies the transfer of one mole of one substance from one thermodynamic environment to the other. Thus, when one mole of benzene is transferred from the thermodynamic environment which prevails in pure benzene to that which prevails in pure alcohol, the change in thermodynamic environment will be measured by the magnitude of the corresponding free energy decrease, which can be shown to be substantially that given by the expression,

$$A = RT \log_e \frac{p_0}{\lim_{x=0} \left(\frac{dp}{dx}\right)} \tag{1}$$

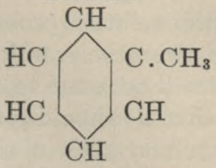
where p_0 is the vapor pressure of the pure benzene and p is its partial vapor pressure from an alcohol solution in which its molecular fraction is x.

2. Ideal Solutions.—We have discussed the character of the solutions formed when benzene is shaken successively with a series of liquids of continuously increasing resemblance to itself. There remains only to consider the limiting case of the solutions formed by mixing with benzene a liquid which resembles it as closely as possible and whose molecules are, therefore, as nearly like those of benzene as possible. Toluene will fulfill these requirements very well as is evident from a comparison of the formulas of the two molecules.

Benzene



Toluene



When we shake these two non-associated (Table VI, 2) liquids together, we find that they not only mix readily with each other in all proportions, but we note also that the process of mixing is not accompanied by any appreciable heat effects or volume changes. The total energy of the system, in other words, is not changed when the two liquids are mixed together. Moreover, this absence of energy changes is found to be generally the case whenever any two very similar non-associated liquids are mixed together and the more nearly the two liquids resemble each other the more exactly, as a rule, does this relation hold true. This behavior is interpreted in terms of our concept of thermodynamic environment by the view that the thermodynamic environments in the two pure liquids are practically identical, and hence on mixing the liquids there is no change in this environment, whatever be the proportions in which they are mixed.[2] That is, a benzene molecule (or a toluene molecule) finds itself in practically the same thermodynamic environment, whether it be surrounded entirely by benzene molecules, or entirely by toluene molecules, or by mixtures of the two molecules in any proportions whatever.

Any solution in which the thermodynamic environment is con-

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[2] The process of mixing in such a case is very analogous to that which occurs when two perfect gases are mixed together in the same volume (XI, 3a). The free energy change which measures the magnitude of the change in thermodynamic environment can be calculated from equation (1) above and has always been found equal to zero when the two liquids resemble each other very closely.

stant, and entirely independent of the relative proportions of the constituents in the solution will be called an **ideal solution.** An ideal solution, like a perfect gas, is strictly, therefore, only a limiting case which is approached the more closely, the more nearly its different molecular components resemble one another. The closest approach of any actual solution to the limiting case of an ideal solution probably occurs when we mix together two liquid hydrocarbons which are optical isomers (I, 2d). Such a mixture will be found to obey all of the laws of ideal solutions so closely that we should probably be unable to detect the slightest deviation and such a solution may, therefore, be considered as an actual example of an ideal solution. It will be readily seen that the following pairs of liquids when mixed together will also form solutions which will be very close to ideal solutions: (1) chlorbenzene and brombenzene; (2) mercury and tin; (3) krypton and xenon; (4) methyl alcohol and ethyl alcohol; (5) holmium and dysprosium; (6) cesium and rubidium.

3. Dilute Solutions.—In general a solution composed of the two substances, A and B, will have a thermodynamic environment different from that which prevails in either pure liquid A or pure liquid B and this thermodynamic environment will vary with changes in the relative amounts of A and B in the solution. Suppose we take any solution composed of A and B and pour into it some pure liquid A. This process is called "diluting the solution with A." As the mole-fraction of A increases and that of B decreases, the thermodynamic environment in the solution approaches gradually that which prevails in pure liquid A and after the degree of dilution has become great enough the molecules of B are so few in number and so far apart that their influence upon the thermodynamic environment of the solution becomes negligibly small. When this condition is reached, further dilution no longer produces any appreciable change in the thermodynamic environment. In other words, for every solution in which one constituent, the solvent (XI, 4) largely predominates over the other, the solute, there exists a degree of dilution beyond which further additions of solvent no longer produce any appreciable effect upon the thermodynamic environment. When the mole fraction of the solvent in any solution is so large that the thermodynamic environment is practically identical with that which prevails in the pure solvent, the solution is called a **"dilute solution,"** or more accurately, a **"sufficiently dilute solution."**

The exact degree of dilution which the solution must have before its thermodynamic environment becomes *practically* constant and hence independent of further increases in the mole fraction of the solvent depends upon the natures of the solvent and the solute. Strictly speaking, the thermodynamic environment never reaches absolute constancy until the solution becomes infinitely dilute, but for practical purposes it becomes sufficiently constant at moderate dilutions and from what has been said above with reference to ideal solutions, it is evident that the more closely the solvent and solute resemble each other, the less dilute does the solution need to be before its thermodynamic environment becomes practically constant. No very accurate general rules can be formulated for deciding just how dilute a solution must be before it may be classed as a "dilute solution," because that is a question which can only be decided by a study of the solution itself. From the knowledge which has been obtained from the study of the behavior of aqueous solutions, however, it is possible to formulate the following general rules which hold for the majority of cases and will give the student a general idea of the concentration range which is usually covered by the term, "dilute solution."

(*a*) Aqueous solutions of most non-electrolytes possess a thermodynamic environment which is practically constant and identical (within say 1 or 2 per cent.) with that which prevails in pure water, as long as the mole fraction of the solute does not exceed about 0.01 (0.5 molal).

(*b*) In a few instances (solutions of the alcohols and the sugars) this limit probably extends as high as 0.04 or 0.05, while in a few others it is very possibly considerably lower than 0.01.

(*c*) In the case of aqueous solutions of strong electrolytes, (I, 2g) in particular, this limit must be placed very much lower, as low as 0.00001 (0.0005 normal) in fact, owing to the powerful effect which ions (I, 2g) exert upon the thermodynamic environment of any solution containing them.

The two groups of solutions which we have just considered, **Ideal Solutions** and **Sufficiently Dilute Solutions,** have the common characteristic of possessing a thermodynamic environment which does not change with variations in the relative amounts of the constituents of the solution, and both groups of solutions obey the *same* set of laws, which we will call the **Laws of Solutions of Constant Thermodynamic Environment** and which we shall now proceed to develop.

REFERENCES

JOURNAL ARTICLES: See Trans. Amer. Electrochem. Soc., **22,** 333 (1912)

CHAPTER XIV

SOLUTIONS IV: THE LAWS OF SOLUTIONS OF CONSTANT THERMODYNAMIC ENVIRONMENT

THE DISTRIBUTION LAWS

1. The General Vapor Pressure Law.—For solutions in which the thermodynamic environment is a constant the function f_A $(T.E.)$ in equation (20, XII) is constant and the equation may therefore be written

$$\left(\frac{\partial p_A}{\partial x_A}\right)_{P,T}=k_A \qquad (1)$$

where p_A is the partial vapor pressure of any molecular species, A, from a solution in which its molecular fraction (XI, 5) is x_A, and k_A is a constant characteristic of the species, A, and of the thermodynamic environment which surrounds it in the solution.

Concerning the quantity, p_A, in this equation it should be remembered that the directly measured vapor pressure above a solution is determined not only by the conditions which exist within the solution but, like any other gas pressure, it is subject to the influences which exist in the vapor itself and which at high pressures or at low temperatures cause the vapor to deviate appreciably from the behavior of a perfect gas (II, 9). If, therefore, the vapor pressure, p_A, in equation (1) is to serve as a suitable measure of the escaping tendency of the molecular species, A, from the solution, it should, strictly speaking, first be corrected for those influences which cause the vapor to deviate from the behavior of a perfect gas. This "corrected vapor pressure" has been called[1] by Lewis[a] the "fugacity" of the mo-

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[1] Lewis [Proc. Amer. Acad. Sci., **37,** 49 (1901)]. The method of making the correction for deviation from the perfect gas law is discussed in this paper and also in a recent paper by Gay [Jour. Chimie Physique, **10,** 197 (1912)], who calls the corrected vapor pressure the "expansibility tension" of the molecular species in question.

In the case of a distribution law involving the vapor phase, if the partial

[a] Gilbert Newton Lewis (1875). Professor of Physical Chemistry and Dean of the College of Chemistry at the University of California.

lecular species, A, in the solution. It is evidently a measure of the tendency of this species to escape from the thermodynamic environment, which surrounds it in the solution, into that condition of *zero thermodynamic environment* which prevails in a perfect gas. The necessary correction which must be applied to the observed vapor pressure in a given case in order to obtain the "fugacity," could be readily calculated, if the constants of the van der Waals' or of the Berthelot equation of state (II, 10a) were known for the vapor in question. As a matter of fact, however, in many cases the magnitude of this correction is so small that it falls within the error of measurement of the vapor pressure itself and can, therefore, be neglected. In general, however, it should be borne in mind that any law of solution which involves the vapor phase may be subject to deviations of the same kind and order of magnitude and from the same sources as those which cause gases to deviate from the perfect gas law (II, 10a).

2. The Vapor Pressure of Ideal Solutions.—By integrating equation (1) we obtain

$$p_A = k_A x_A + I \qquad (2)$$

When $x_A = 0$, $p_A = 0$ also, and hence the integration constant, I, is zero. When $x_A = 1$, $k_A = p_{0_A}$, the vapor pressure of pure liquid A at the same temperature and pressure. Equation (2), therefore, becomes:

$$p_A = p_{0_A} x_A \qquad (3)$$

or stated in words: The partial vapor pressure of any molecular species above an ideal solution is equal to its vapor pressure as a pure liquid at the same temperature and pressure multiplied by its molecular fraction in the solution. In other words the partial vapor pressure of any molecular species from an ideal solution is a linear function of its molecular fraction in that solution.

vapor pressure employed has been obtained (as is usually the case) by calculation from the percentage composition of the vapor in equilibrium with the solution on the assumption that the vapor behaves like a perfect gas, the vapor pressure so calculated is, thereby, usually automatically "corrected" for the effect of the influences present in the gas phase and when substituted in the distribution law in question usually shows good agreement with the law. This is the case with the data exhibited in Fig. 19.

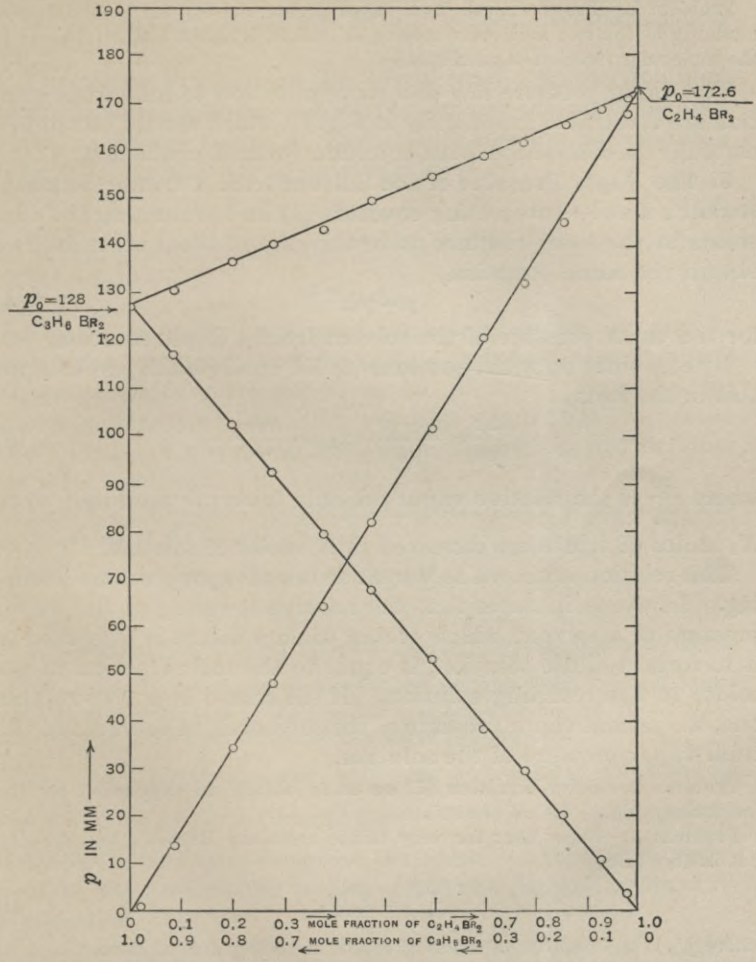

FIG. 19.—The Vapor Pressure Diagram for an Ideal Solution. The two intersecting straight lines in the figure are the graphs of the theoretical equation, $p = p_0x$, using the values of p_0 indicated on the right and left hand margins respectively. The upper curve is the theoretical total vapor pressure curve. The small circles represent the observed vapor pressures at 85° for the system proplyene bromide—ethylene bromide as measured by Zawidski. [Z. physik. Chem. **35,** 129 (1900)]. This system is evidently very close to an ideal solution in its behavior.

Problem 1.—Prove that the *total* vapor pressure above an ideal solution made up of the two molecular species, A and B, is also a linear function of the molecular fraction of each species.

The vapor pressure law and its application to an actual solution are illustrated graphically in Fig. 19, which should be studied carefully in connection with equation (3) and problem 1.

3. The Vapor Pressure of the Solvent from a Dilute Solution. Raoult's Law.—Integrating equation (1) and evaluating the constants in the same manner as in the case of ideal solutions, we obtain the same equation,

$$p = p_0 x \tag{4}$$

for the vapor pressure of the solvent from a dilute solution.

By combination with equations (2, XI), and (9, XII) we can put this in the form,

$$\frac{\Delta p}{p_0} = \frac{p_0 - p}{p_0} = x_1 = \frac{N_1}{N + N_1} \tag{5}$$

where $\frac{\Delta p}{p_0}$ is the relative vapor pressure lowering produced when N_1 moles of solute are dissolved in N moles of solvent.

This relation is known as **Raoult's[a] law of vapor pressure lowering.** In words it states that the relative lowering of the vapor pressure of a solvent, which occurs when a solute is dissolved in it to form a dilute solution, is equal to the mole fraction of the solute in the resulting solution. If the solute is a non-volatile one, the partial vapor pressure of the solvent is, of course, also the total vapor pressure of the solution.

Problem 2.—Solve equation (5) so as to obtain an expression for the molecular weight, M_1, of the solute.

Problem 3.—Show that for very dilute solutions Raoult's law may be put in the form,

$$\frac{\Delta p}{p_0} = k_p \underline{N}_1 \tag{6}$$

where $\underline{N}_1$ is the number of moles of solute in 1000 grams of solvent and k_p is a constant which depends only upon the nature of the solvent.

For solutions which are so dilute that equation (6) holds with sufficient accuracy, the relative vapor pressure lowering is independent of the temperature.

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[a] François Marie Raoult (1832–1901). Professor of Chemistry in the University of Grenoble. Made important contributions to the methods of molecular weight determination in solution.

Problem 4.—Calculate the relative vapor pressure lowering produced when one formula weight of diphenyl ($C_{12}H_{10}$) is dissolved in 1000 grams of benzene.

4. The Vapor Pressure of the Solute from a Dilute Solution. Henry's Law.—To obtain an expression for the partial vapor pressure, p_A, of any solute, A, from a dilute solution, we have only to integrate equation (1) again which gives

$$p_A = k_A x_A + I \tag{7}$$

If $x_A = 0$, $p_A = 0$ and hence I = 0. The desired relation is, therefore,

$$p_A = k_A x_A \tag{8}$$

where x_A is the mole fraction of the solute species, A, and k_A is the *constant characteristic of the solute A and of the thermodynamic environment which surrounds it in the solution.* Equation (8) is known as **Henry's[a] Law.** In words it states that the partial vapor pressure of a solute from a dilute solution is proportional to its mole fraction in the solution.

Problem 5.—Show that if the solution is dilute enough, Henry's law may be put in either of the following forms:

$$p_A = const. \times \underline{N}_A \tag{9}$$

$$p_A = const. \times C_A \tag{10}$$

$$C'_A = const. \times C_A \quad \text{and (if } p = \text{const.)} \ x'_A = \text{const.} \times x_A \tag{11}$$

where $\underline{N}_A$ and C_A are the weight-molal and volume-molal concentrations (XI, 5), respectively, of A in the solution and C'_A and x'_A its volume concentration and mole fraction in the gas above the solution.

Table XIV illustrates the behavior of aqueous solutions of carbon dioxide toward Henry's Law. The ratio, $\frac{C'}{C}$, is usually called the "*solubility of the gas in the liquid.*" Another quantity known as the "*absorption coefficient*" of the gas and defined by the equation

$$\alpha = \frac{273.1\ C'}{TC} \tag{12}$$

where T is the absolute temperature, is frequently employed in recording data on solubility of gases.

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[a] William Henry, F. R. S. (1774–1836). Son of the chemist Thomas Henry. A physician and manufacturing chemist in Manchester, England. His work on the solubility of gases was published in 1803.

TABLE XIV

Partial Pressure and Solubility of CO_2 in Water at 25°. Illustrating Henry's Law, $\frac{C'_{CO_2}}{C_{CO_2}}=\text{const.}$

Measurements by Findlay, Creighton, and Williams [J. Chem. Soc. **97**, 538 and **103**, 637].

P_{CO_2}, mm.	265	385	485	660	760	820	955	1060	1150	1240	1350
$\frac{C'_{CO_2}}{C_{CO_2}}$	0.817	0.813	0.816	0.817	0.817	0.816	0.817	0.818	0.818	0.819	0.820

Problem 6.—Air contains 0.04 per cent. by volume of CO_2. What is the concentration of carbon dioxide in water which is in equilibrium with air at 25° and 1 atm.? (Use Table XIV.)

5. The Distribution Law for Dilute Solutions.—If we take a dilute solution of some substance in solvent, 1, and shake this solution with another solvent, 2, with which the first solvent is immiscible, then some of the solute molecules will pass from the first to the second solvent until finally a state of equilibrium is reached. The solute is now said to be in *distribution equilibrium* between the two solvents and hence according to the Second Law of Thermodynamics (see the last paragraph of X, 10), it must have the same vapor pressure from both solutions.

Problem 7.—Prove by the methods of Section 10, Chapter X, that the two vapor pressures must be equal in such a case.

But by Henry's Law (equation 8) the vapor pressure, p_1, of the solute molecules above solvent 1, is

$$p_1 = k_1 x_1 \tag{13}$$

and that, p_2, above solvent 2, is

$$p_2 = k_2 x_2 \tag{14}$$

and since $p_1 = p_2$, we have

$$\frac{x_1}{x_2} = \frac{k_2}{k_1} = k_D \tag{15}$$

where k_D is the so-called *distribution coefficient* or *distribution constant* of the molecular species in question between the two solvents. Stated in words: When any molecular species in dilute solution is in distribution equilibrium between two immiscible solvents the ratio of its mole fractions in the two solvents is always equal to a constant whose value is characteristic of the species in question and of the two thermodynamic environments which respectively exist in the two solvents.

Problem 8.—Show that if the two mole fractions are small enough equation (15) can be put in either of the following forms:

$$\frac{\underline{N}_1}{\underline{N}_2} = const. \tag{16}$$

$$\frac{C_1}{C_2} = const. \tag{17}$$

where $\underline{N}$ and C are respectively the weight-molal and the volume-molal concentrations in the two solvents.

The data in Table XV illustrate the behavior of $HgBr_2$ in distribution equilibrium between water (W) and benzene (B).

Table XV

Distribution of $HgBr_2$ between water and benzene at 25°. Illustrating the Distribution Law, $C_1/C_2 = const.$, in the case of two liquid phases. (Cf. XIV, 15.)

Measurements by Sherrill [Z. phys. Chem. **44,** 70 (1903)].

C_W =	0.00320	0.00634	0.0115	0.0170
C_B =	0.00353	0.00715	0.0130	0.0194
C_W/C_B =	0.906	0.886	0.880	0.876

Although in the above statement and derivation of the distribution law we have employed liquid solutions, the law is a more general one, one in fact which governs the distribution equilibrium of any molecular species between any two phases whatever, be they crystalline, liquid or gaseous, provided only that the thermodynamic environment in each phase does not change with the mole fraction of the solute in that phase, that is, provided that the solution in each phase is a "sufficiently dilute solution" (XIII, 3). Henry's law as expressed by equation (11) is evidently only a special case of this general distribution law.

Problem 9.—At 25° the distribution ratio of Br_2 between carbon tetrachloride and water is $\frac{C_C}{C_W} = 38$. The partial pressure of Br_2 above a 0.05 molal solution of it in water at 25° is 50 mm. If 1 liter of this solution is shaken with 50 c.c. of carbon tetrachloride, what will be the pressure of the bromine above the carbon tetrachloride phase.

Problem 9a.—At 25° the solubility of iodine, I_2, in CCl_4 is 30.33 grams per liter and in water 0.00132 moles per liter. One liter of CCl_4 containing 25 grams of I_2 is shaken with 3 liters of water at 25° until equilibrium is established. How many grams of iodine will be found in the water layer?

OSMOTIC PRESSURE AND OSMOSIS[3]

6. The General Osmotic Pressure Law.—By dividing equation (1) by its integral, $p_A = k_A x_A$, we eliminate the constant, k_A, and obtain

$$dp_A = p_A \frac{dx_A}{x_A} \tag{18}$$

By combining this equation with equation (15, XII) so as to eliminate dp, and putting RT in place of pv_0 in the result we have the osmotic pressure law for solutions of constant thermodynamic environment, namely,

$$d\Pi_A = \frac{-RT}{V_{0A}} \frac{dx_A}{x_A} = \frac{-RT}{V_{0A}} d\log_e x_A \tag{19}$$

This expresses the osmotic pressure of the solution *referred to constituent*, A, (XII, 7) whose molal volume as a pure liquid is V_{0A} and whose mole fraction in the solution is x_A.

If we assume that the substance A as a pure liquid is incompressible, then V_{0A} is a constant independent of Π and the general integral of equation (19) is

$$\Pi_A = -\frac{RT}{V_{0A}} \log_e x_A \tag{20}$$

the integration constant being obviously zero. This equation expresses the general connection between the osmotic pressure of an ideal solution and its composition.

The same equation also applies to dilute solutions, if we understand that the solvent is the constituent which is present as the pure liquid (cf. the definition of osmotic pressure, XII, 7), and with this understanding we may drop the subscript, A, and write

$$\Pi = -\frac{RT}{V_0} \log_e x \tag{21}$$

x being the mole fraction of the solvent in the solution and V_0 its molal volume as a pure liquid at the temperature T.

7. Direct Osmotic Pressure Measurements.—The pressure difference necessary to prevent osmosis through a perfectly semipermeable (XII, 7) membrane is equal to the osmotic pressure and by determining this pressure difference for a given solution the osmotic pressure is thus directly measured. Membranes which approximate perfect semipermeability have thus far been obtained only in the case of a few aqueous sugar solutions and accurate measurements of osmotic pressure by this method are consequently very few in number.

In Table XVI below are shown some results obtained by Morse[a] and his associates for the osmotic pressures of cane-sugar solutions at 25°. These investigators employed membranes of cupric ferrocyanide deposited in the pores of a porous earthenware cell. The sugar solution was placed in the interior of the cell which was then surrounded by water. The pressure upon the solution was then increased until it was just sufficient to prevent the passage of water into or out of the cell through the cupric ferrocyanide membrane.

It is not without interest to compare the values of the osmotic pressure obtained in this way with those calculated from the theoretical equation for an ideal solution (21), although for the solutions employed by Morse the calculation cannot be carried out without making several of assumptions. In the first place the osmotic pressure measured by Morse is that defined by equation (13, XII) while that which appears in the equation for an ideal solution (21) is defined by equation (12, XII). For cane sugar solutions at 25°, however, the two quantities Π and Π' do not differ by more than 1.6 per cent. for the concentration range covered by the table. Another difficulty in applying equation (21) to these solutions is that this equation assumes that the "pure solvent," that is, the constituent to which the membrane is permeable, is composed of only one species of molecule, a condition which is not fufilled in the case of water. A third difficulty lies in the fact that for cane-sugar solutions the molecular formula of the solute in the solution is not known with certainty, for the sugar molecules very probably become hydrated when they dissolve in water.

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[a] Harmon Northrup Morse (1848–). Professor of Inorganic and Analytical Chemistry at Johns Hopkins University.

TABLE XVI

Comparison of the measured values of the osmotic pressure, Π', of aqueous cane-sugar solutions at 25° with the values calculated from the relation,

$$\Pi = \frac{-RT}{V_0}\log_e \frac{N}{N+N_1} = \frac{-0.08207\times(273.1+25)\times 2.303}{\frac{1.00294\times 18.015}{1000}}\log_{10}\frac{N}{N+N_1}$$

Measurements by Morse and Associates, Amer. Chem. Jour. **45,** 600 (1911)

Weight formal concentration of $C_{12}H_{22}O_{11}$ $\underline{N}_1$	Observed osmotic pressure (in atmospheres) Π'	Calculated osmotic pressure assuming the formula $C_{12}H_{22}O_{11}$ Π_1	Calculated osmotic pressure assuming the formula $C_{12}H_{22}O_{11}\cdot 6H_2O$ Π_2
0.09924	2.63	2.4	2.4
0.1985	5.15	4.8	4.9
0.2978	7.73	7.2	7.5
0.4962	12.94	12.0	12.7
0.5954	15.62	14.4	15.4
0.6946	18.43	16.8	18.2
0.7929	21.25	19.2	21.1
0.8931	24.13	21.6	23.9
0.9924	27.05	24.0	26.7

If it be assumed that the sugar is not hydrated and that water has the molecular weight 18, then the mole fraction of the water in a solution containing $\underline{N}_1$ moles of sugar ($C_{12}H_{22}O_{11}$) per 1000 grams of water would be

$$x = \frac{1000}{18} \div \left(\frac{1000}{18} + \underline{N}_1\right) \tag{22}$$

If values of x calculated in this way be substituted in the theoretical equation (21), the values of Π_1 thus obtained are shown in column 3 of Table XVI.

These values do not agree very well with the experimental ones. Part of the disagreement is undoubtedly due to the fact that water is not a pure substance with a molecular weight in the liquid state of 18. The disagreement is probably too great to be accounted for by this fact alone, however, for the value assumed for the molecular weight of water appears in the equation in such a way that for moderate concentrations it cancels itself out approximately, as can be seen by a careful examination of equations (21) and (22). Most of the difference between the calculated and the observed values can probably be attributed to an erroneous assumption with regard to the molecular weight of sugar when dissolved in water. Instead of remaining unhydrated, it is probable that the sugar molecules unite with some of the water to form a hydrate. If the number of water molecules which unite in this way with one molecule of sugar is W, then the mole fraction of the *free water* as computed from equation (22) above would evidently be

$$x = \left(\frac{1000}{18} - W\underline{N}_1\right) \div \left(\frac{1000}{18} - W\underline{N}_1 + \underline{N}_1\right) \tag{23}$$

If we assume $W = 6$ and substitute values of x computed from equation (23) in equation (21), we obtain the values of Π_2 given in the column 4 of Table XVI. These values show good agreement with the experimental ones and this agreement may be taken as evidence that the molecules of cane sugar in aqueous solution are on the average each hydrated with approximately 6 molecules of water. The molecular formula of the solute in solution would, therefore, be $C_{12}H_{22}O_{11} \cdot 6H_2O$.

We have mentioned the fact (XII, 7) that the osmotic pressure of any solution can be thermodynamically calculated from the other colligative properties of the solution. As an example of the values thus obtained in the case of cane sugar solutions at 0°, Table XVII is given. The "*calculated*" values were computed from the freezing points of the solutions by means of the integral of equation (17, XII). The "*observed*" values were directly measured by Morse and his associates.

Problem 9.—A 1 per cent. solution of dextrin in water has at 16° an osmotic pressure of 16.6 cm. of mercury. Calculate the molecular weight of the solute. (Use the van't Hoff equation (28).) To what fraction of a degree would it be necessary to know the freezing point of this solution in order to determine the molecular weight of dextrin to 1 per cent. by the freezing point method? (Use equation (51).)

This problem illustrates the application of the osmotic pressure law to the determination of the molecular weight of substances whose molecules are made up of a very large number of atoms.

Molecules such as those of dextrin and albumin are, in fact, so large that solutions of these substances resemble colloidal solutions in many respects and are usually classed with such solutions for the purposes of systematic treatment. Owing to the small molal concentration of many of these solutions, the freezing point lowering is so small that it cannot be measured with sufficient accuracy to give a satisfactory value for the molecular weight of the solute. Moreover the freezing point is liable to be seriously affected by the presence of traces of impurities. It is with such solutions as these that the osmotic pressure method is of particular value for molecular weight determinations. Membranes quite impermeable to the large solute molecules, and sufficiently strong to withstand the small pressures involved, are comparatively easy to secure and these membranes are usually permeable to many of the impurities present in the solution and hence the measured osmotic pressure is not influenced by these impurities.

TABLE XVII

Comparison of the osmotic pressures of cane sugar solutions at 0° determined by direct measurement, with the osmotic pressures thermodynamically calculated from the freezing point lowerings by means of the integral of equation (17, XII) which for aqueous solutions may be written, $\Pi = 12.06(\Delta t_F - 1.78 \times 10^{-3}\Delta t_F^2 - 2.5 \times 10^{-6}\Delta t_F^3)$.

Measurements by Morse and Associates, Amer. Chem. Jour. **45,** 600 (1911). Calculations according to Lewis, Jour. Amer. Chem. Soc. **30,** 671 (1908).

Weight-formal concentration of $C_{12}H_{22}O_{11}$ $\underline{N}_1$	Freezing point lowering Δt_F	Observed osmotic pressure Π'	Calculated osmotic pressure Π
0.09924	0.195	(2.46)	2.35
0.1985	0.392	4.72	4.73
0.2978	0.585	7.08	7.05
0.4962	0.985	11.9	11.9
0.5954	1.19	14.4	14.4
0.6946	1.39	16.9	16.8
0.7929	1.62	19.5	19.5
0.8931	1.83	22.1	22.0
0.9924	2.07	24.8	24.9

8. The Van't Hoff Equation.—In the comparisons given in Table XVI we employed the general osmotic pressure law in the form,

$$\Pi = -\frac{RT}{V_0} \log_e x \qquad (24)$$

If the mole fraction of the solute is small enough, however, this equation may be rearranged into a more convenient form for calculation. In place of x we may put $1 - x_1$ (eq. 2, XI), where x_1 is the mole fraction of the solute in the solution. This gives,

$$\Pi = -\frac{RT}{V_0} \log_e (1 - x_1) \qquad (25)$$

and by expanding the logarithm into a series with the help of Maclaurin's Theorem we have

$$\Pi = \frac{RT}{V_0}(x_1 + \tfrac{1}{2}x_1^2 + \tfrac{1}{3}x_1^3 + \cdot \cdot \cdot \cdot \cdot) \qquad (26)$$

If the mole fraction of the solute is *small enough*, its higher powers may be neglected in comparison with its first power and we can write

$$\Pi = \frac{RT}{V_0}x_1 = \frac{RT}{V_0} \frac{N_1}{N + N_1} \qquad (27)$$

and if we may neglect N_1 in comparison N in the denominator of the right-hand member and write V in place of NV_0, this equation becomes

$$\Pi V = N_1 RT \qquad (28)$$

where N_1 is evidently the number of moles of solute in V liters of solvent at $T°$. As the solution becomes more and more dilute V becomes practically identical with the volume, V_s, of the solution containing N_1 moles of solute. When this is true we have

$$\Pi V_s = N_1 RT \text{ or } \Pi = C_1 RT \qquad (29)$$

The formal resemblance between equation (29) and the perfect gas law is obvious and for this reason it is possible to say that the osmotic pressure of an *extremely dilute* solution is numerically equal to the pressure which the solute molecules would exert as a gas, if they occupied the same volume as they do in the solution and had the same temperature. This is the form in which the osmotic pressure law was first stated by van't Hoff in

1886 and equation (29) is known as **van't Hoff's law of osmotic pressure.** Now the pressure of a gas is due to the impacts of the molecules of the gas upon the walls of the containing vessel and owing to the formal resemblance between van't Hoff's osmotic pressure law and the equation of state of a perfect gas, many persons have held the view that the osmotic pressure of a solution is a real pressure existing within the solution and caused by the impacts of the solute molecules against any retaining surface. In order to make clear the illogical character of such a view we will consider in some detail the molecular kinetic interpretation of the process of osmosis.

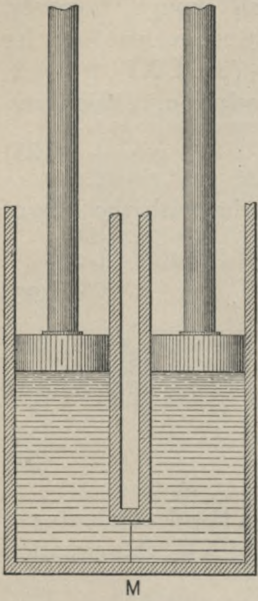

Fig. 20.

9. The Molecular Kinetic Interpretation of the Process of Osmosis. (*a*) **Osmosis in the Case of Ideal Solutions.**—Fig. 20 represents two vessels each filled with a liquid A which for convenience we will designate as our solvent. Each vessel is provided with a piston by means of which the total pressure upon the liquid may be varied at will. The two vessels are connected by a tube fitted with a membrane, *M*, of infinitesimal thickness which allows the molecules of A to pass through it, but which is impermeable to every other species of molecule. Let both vessels be initially under the same pressure and at the same temperature.

The molecules of *A* being in constant motion will strike the membrane, *M*, from both sides and hence will pass through it in both directions, but since the concentrations of the A molecules and the temperature, pressure and other conditions are the same in both vessels, equal numbers of molecules will strike both sides of the membrane in unit time and hence the quantities of A passing through the membrane will be the same in the two directions. Suppose now that we dissolve in the liquid in the right-hand vessel some substance, B, which forms an ideal solution with A. Since there are now fewer molecules of A *per unit volume* in the right-hand vessel, the number of these molecules which can strike the semipermeable membrane from the right in unit time must be less than the number which strike it from the left and hence there must be a flow of A from left to right through the membrane. In other words osmosis must occur.

This osmosis might be stopped (1) by raising the temperature of the right-hand vessel or by lowering that of the left-hand vessel, or it might also be stopped (2) by raising the pressure on the right-hand vessel or by lowering that on the left-hand vessel. If the second method is employed the pressure difference necessary to make the rates of passage of the A molecules through the membrane the same in the two directions, is evidently what we have defined (XII, 7) as the osmotic pressure of the solution.[2] One effect of increasing the pressure upon any liquid is to force the molecules closer together and, therefore, to increase the repulsive forces acting between them and hence to increase the vigor of their molecular impacts against any surface. By increasing the pressure upon the right-hand vessel, therefore, the vigor of the impacts of the A molecules against the semipermeable membrane (and to a slight extent the concentration of these molecules as well) would be increased and the number of molecules which are able to pass through the membrane per unit time would consequently be increased. This is the most probable molecular kinetic interpretation of the process of osmosis and of the way in which the change of pressure on one side of the membrane brings the osmosis to a stop, in the simple case of an ideal solution.

As the mole fraction of the B molecules in the right-hand vessel of Fig. 20 is increased the osmotic pressure increases in accordance with the integral of equation (19) and, as this integral shows, the osmotic pressure must approach *infinity* as the mole fraction of B approaches unity. This statement holds true regardless of the natures of A and B. In other words no pressure difference, however great, would be able to prevent the passage of A molecules from pure A on the left of the membrane into pure B on the right.

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[2] Evidently an "osmotic temperature" for the solution might be similarly defined, if one wished to do so.

(*b*) **Osmosis in General.**—In the simple case of the ideal solution just considered we have seen that the solvent would flow through the semipermeable membrane into the solution merely because there is a greater number of solvent molecules per unit volume in the pure solvent than in the solution and hence the number of molecules striking the membrane from the solvent side will naturally be the greater. In other words the osmosis in such a case would be a purely kinetic phenomenon and quite analogous to the passage of hydrogen gas through a palladium wall into a gaseous mixture containing hydrogen at a smaller concentration (Cf. II, 6). In general, however, the phenomenon of osmosis is a more complex process, one which is probably quite appreciably influenced by the attractive forces (neutralized in the cases of ideal solutions) which act between the molecules in the interior of the liquid. Thus when a strong aqueous sugar solution is separated from pure water by a membrane permeable only to the water, the rate of osmosis might be very appreciably influenced by attractive forces acting between the sugar molecules on one side of the membrane and the water molecules on the other side of the membrane, or in the interior of the membrane if the latter is of appreciable thickness. The presence of such forces would affect also the pressure difference which must be established on solvent and solution respectively in order to stop the osmosis. This is only another way of stating that the osmotic pressure of a solution is in general a function of the thermodynamic environment prevailing within the solution. (Cf. XIII, 1.)

In the above interpretation of the process of osmosis it will be noticed that we have said nothing about any *pressure exerted against the semipermeable membrane* by the molecules of the solute, nor is it necessary that we should. Such a pressure would undoubtedly exist, for the membrane is constantly being bombarded by these solute molecules, but this pressure *is not* the osmotic pressure of the solution. The osmotic pressure of a solution is, in fact, not a real pressure exerted by something within solution, but is instead an abstraction, representing simply the pressure difference which would have to be established upon solution and pure solvent respectively in order that the solvent should have the same escaping tendency from both of them. It is thus a definite physical quantity quite independent of semipermeable membranes, osmosis or molecular theory of liquids. The partial pressure of the solute molecules against the semipermeable membrane has, however, been frequently given as the cause of osmosis and has been identified with the osmotic pressure. To what extent this is justifiable will become evident from the following considerations.

(*c*) **Thermal Pressure and Diffusion Pressure.**—When a dilute solution of B in A in the right-hand vessel of Fig. 20 is separated from pure A in the left-hand vessel by a membrane permeable only to A, the molecules of B which are constantly striking the right-hand side of this membrane will exert against it a certain partial pressure, p_D, which we will call the diffusion pressure of these molecules, since it is evidently a measure of the tendency of the solute to diffuse into the pure solvent, the diffusion being in the above case prevented by the presence of the membrane. The following molecular kinetic analysis of the conditions at the surface of the membrane will aid us in appreciating the nature of some of the factors which determine the magnitude of this diffusion pressure of the solute molecules.

Let both liquids be under atmospheric pressure and consider the layer of B molecules which at any moment are just about to strike the membrane from the right. If these molecules were not subject to any attractive forces from their neighbors, they would exert against the membrane a pressure, p_T, which will be called their thermal pressure and which would be equal to the pressure exerted by an equal number of molecules of a gas at the same temperature and the same effective concentration. As a matter of fact, however, the layer of B molecules next the membrane will be subject to a pull backward by both the A and the B molecules which are behind them and to a pull forward by the A molecules on the other side of the membrane. These different attractive forces will influence the force with which the B molecules strike the membrane, and will thus be a determining factor in the effective pressure which these molecules will be able to exert against the membrane. If we call p_{A} and p_{B} the backward pulls (in pressure units) exerted by the A and the B molecules in the solution, and p'_{A} the forward pull exerted by the A molecules on the other side of the membrane, then the actual pressure, p_D, which the B molecules will exert against the membrane, when they strike it, will be

$$p_D = p_T + p'_{\mathrm{A}} - (p_{\mathrm{A}} + p_{\mathrm{B}}) \tag{30}$$

For the thermal pressure, p_T, we might write

$$p_T = \frac{N_{\mathrm{B}}RT}{(V-b)} = C_{Cor.}\,RT \tag{31}$$

where $C_{Cor.}$ is the molal concentration of the B molecules, corrected for the space actually filled by these molecules, the correction being made according to the method of reasoning employed by van der Waals in correcting the gas law for high pressures. (Cf. II, 10a.) $C_{Cor.}$ will be called the effective concentration of the B molecules.

In the limiting case of an ideal solution $p'_{\mathrm{A}} = p_{\mathrm{A}} + p_{\mathrm{B}}$ for all concentrations and in the case of any dilute solution, as the concentration of the solute, B, decreases and approaches zero, p_{B} approaches zero and p'_{A} approaches p_{A}, so that here also $p'_{\mathrm{A}} = p_{\mathrm{A}} + p_{\mathrm{B}}$. In words, the diffusion pressure of the molecules of the solute in an ideal solution or in an infinitely dilute solution is equal to their thermal pressure and hence is equal to the pressure which they would exert in the gaseous state at the same temperature and the same effective concentration.

If we start with a solution in which the concentration of the solute is small, then as we gradually increase it, the value of p_D (equation 30) will evidently always remain finite and, if the solution is an ideal one, $p_D = p_T = C_{Cor.}RT$ for all values of the concentration. If the solution is not an ideal solution, the value of p_D is equal to CRT for small concentrations, but as the concentration of the solute increases, p_D will at first increase more slowly than $C_{Cor.}RT$, owing to the fact that $p_{\mathrm{A}} + p_{\mathrm{B}}$ in equation (30) is greater than p'_{A}. As the concentration of the solute continues to increase, however, a point may be reached where p'_{A} is greater than $p_{\mathrm{A}} + p_{\mathrm{B}}$. If this is true, the value of p_D might for a time increase faster than $C_{Cor.}RT$. In other words the variation of p_D with the concentration is in general not predictable between infinite dilution and pure solute. When the mole fraction of the solute in the right-hand vessel becomes unity, however, p_{A} obviously becomes zero and we have, $p_D = p_T + p'_{\mathrm{A}} - p_{\mathrm{B}}$. Beyond the fact that p_D under these conditions must still be a finite quantity, we cannot make any general statement with regard to its magnitude or even with regard to its sign, although these can usually be determined in any specific case.

In the preceding discussion we have considered the conditions which exist on the two sides of the membrane when both the solution and the pure solvent are under the same total pressure and at the same temperature. If the pressure or temperature of the solution be altered, however, there will be corresponding changes in the thermal pressure and the diffusion pressure of the solute molecules. Increase of pressure upon the solution will cause a corresponding increase in the diffusion pressure of the solute molecules and their diffusion pressure can be made numerically equal to the osmotic pressure, Π' defined by equation (13), by putting the solution under the pressure, P, also defined by that equation. In other words for the special case when a solution is in osmotic equilibrium with the pure solvent, the diffusion pressure of the solute molecules is equal in magnitude to the osmotic pressure, Π', of the solution.

(*d*) **Summary.**—We may sum up our discussion in the following terms. Osmotic pressure, thermal pressure, and diffusion pressure are three quite distinct quantities and should be recognized as such. Briefly they are defined and described as follows:

1. *Osmotic Pressure.*—The osmotic pressure of a solution is the pressure difference which must be established upon the solution and the pure solvent respectively, in order to make the escaping tendency of the solvent the same from both of them. The osmotic pressure is, therefore, not a real pressure existing within the solution but is a definite physical quantity quite independent of osmosis, semipermeable membranes or molecular theory. It is connected with the other colligative properties of the solution by definite relations which can be deduced by purely thermodynamic reasoning. For dilute solutions the osmotic pressure becomes in the limit equal to CRT where C is the concentration of the solute, but as the concentration increases the *osmotic pressure approaches infinity as its upper limit.*

2. *Thermal Pressure.*—Every molecular species in a solution possesses the unordered heat motion of all fluid molecules and by virtue of this motion its molecules may be considered as having a

corresponding pressure, p_T, called their thermal pressure. For dilute solutions of the species in question this pressure will be equal to CRT but as the concentration of the molecular species increases the value of p_T also increases and *approaches a finite but usually very large upper limit*, the thermal pressure of the molecules in the pure liquid solute. If van der Waals' equation held for the liquid. the thermal pressure would be equal to

$$\frac{N_1RT}{(V-b)}.$$

3. *Diffusion Pressure.*—The partial pressure which the solute molecules in any solution would exert against a membrane permeable only to the solvent is called their diffusion pressure, p_D. For dilute solutions the diffusion pressure is equal to CRT but as the concentration of the solute increases, the diffusion pressure *remains finite for all values of C* and reaches a definite limiting value whose magnitude and sign depend upon the temperature, the external pressure and the attractive forces which are acting in the interior of the liquid.

The way in which the three quantities, Π, p_T and p_D, change with the mole fraction of the solute is illustrated graphically in Fig. 21.

The above rather detailed treatment of these three quantities has been deemed advisable because of the great confusion regarding them which exists in the literature. The term osmotic pressure is loosely used to designate all three quantities, frequently without any appreciation of the difference between them. Osmotic pressure is frequently spoken of as the "cause of osmosis," and attempts are made to calculate the diffusion pressure from the freezing point. Neither the diffusion pressure nor the thermal pressure can be calculated from the freezing point, as there is no known relation connecting them. The osmotic pressure can be so calculated, however, (see Table XVII) and if the concentration of the solute in the solution is so small that the value of its diffusion pressure and the value of the osmotic pressure are within say 0.1 per cent. of each other, then the value of the diffusion pressure would obviously also be known within that limit. The calculation of diffusion pressure in such a manner, however, obviously involves an *a priori* knowledge of

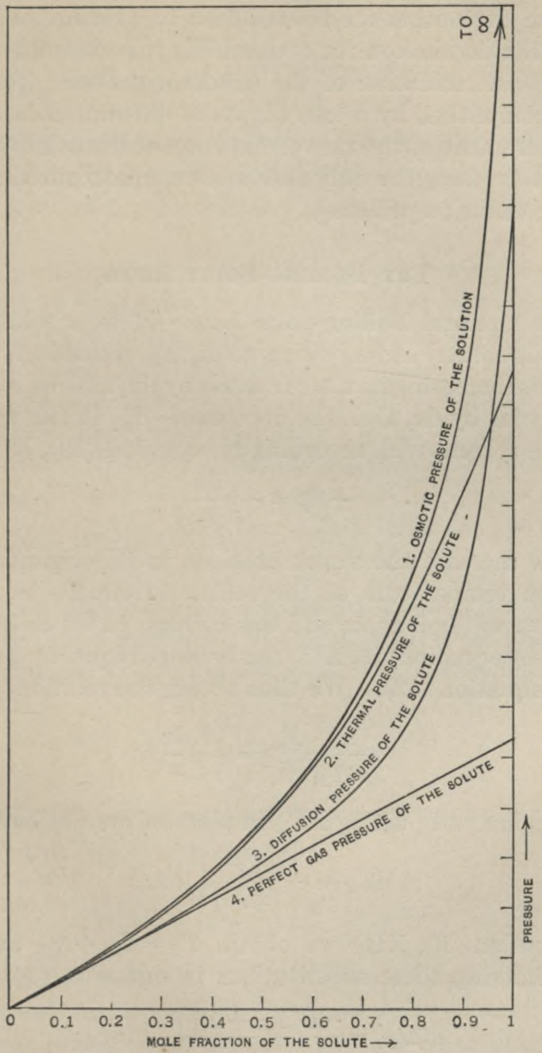

FIG. 21.—Illustrating the Difference in the Quantities, Osmotic Pressure, Thermal Pressure, Diffusion Pressure and Perfect Gas Pressure for a Solution under Constant Pressure and at Constant Temperature.

the amount by which the numerical values of the two pressures differ from each other for the solution in question and there is no very reliable method for determining this except by means of the direct determination of the diffusion pressure itself, which can be accomplished by means of rate-of-diffusion measurements. The measurement of the rate of diffusion of the solute in a given solution is, in fact, the only safe and certain method for determining its diffusion pressure.

THE BOILING-POINT LAWS

10. The General Boiling-point Law.—If to a solution (of a non-volatile solute) at its boiling point, T_B, we add $\mathrm{d}N_1$ moles of solute, thus increasing its mole fraction by $\mathrm{d}x_1$ and decreasing that of the solvent by $\mathrm{d}x$, then the decrease, $-\mathrm{d}p$, in the vapor pressure of the solvent will, according to equation (18), be

$$-\mathrm{d}p = -p\frac{\mathrm{d}x}{x} \tag{32}$$

If we now increase the vapor pressure to its original value by raising the temperature of the solution from T_B to $T_B + \mathrm{d}T_B$, the solution will boil again and this increase in vapor pressure as expressed by equation (16, XII) can be placed equal to the decrease given by equation (32). We thus obtain the relation,

$$\frac{L_v}{v_0 T_B}\mathrm{d}T_B = -p\frac{\mathrm{d}x}{x} \tag{33}$$

or rearranging and putting RT_B in place of pv_0, we have

$$\mathrm{d}T_B = -\frac{RT_B{}^2}{L_v}\,\mathrm{d}\log_e x \tag{34}$$

From equation (10, XII) we obtain $T_B = T_{B_0} + \Delta t_B$ and $\mathrm{d}T_B = \mathrm{d}(\Delta t_B)$. Making these substitutions in equation (34) we have

$$\mathrm{d}(\Delta t_B) = \frac{-R(T_{B_0} + \Delta t_B)^2}{L_v}\,\mathrm{d}\log_e x \tag{35}$$

In order to integrate this equation it is first necessary to express L_v as a function of Δt_B which can be done thermodynamically in terms of the specific heats of the pure solvent in the liquid and vapor states respectively.

If L_v in a given case can be regarded as practically constant over the range covered by Δt_B, the integral would be

$$\log_{10} x = \frac{-0.4343 L_v}{R T_{B_0}} \frac{\Delta t_B}{T_B} \tag{36}$$

In Fig. 22 a comparison is shown between the values of Δt_B calculated from the general integral of equation (35) and those obtained by direct measurement in the case of some solutions in benzene.

11. Dilute Solutions.—With the aid of Maclaurin's Theorem the integral of equation (35) can be obtained in a form in which the boiling-point raising, Δt_B, is expressed as a power series in the mole fraction, x_1, of the solute (cf. equation 26) and if x_1 is small enough the terms of the series which contain its higher powers can be neglected in comparison with the term containing its first power. If this is done, the series-integral reduces to the expression,

$$\Delta t_B = \frac{R T_{B_0}^2}{L_v} x_1 = \frac{R T_{B_0}^2}{L_v} \frac{N_1}{N + N_1} \tag{37}$$

This is frequently the most convenient form of the equation to employ for dilute solutions. If the solution is so dilute that N_1 can be neglected in comparison with N in the denominator, we may write

$$\Delta t_B = \frac{R T^2_{B_0}}{L_v} \frac{N_1}{N} \text{ (approx.)} \tag{38}$$

and if we let $\underline{N}_1$ be the number of moles of solute in 1000 grams of solvent this equation becomes

$$\Delta t_B = \left(\frac{M R T^2_{B_0}}{1000 L_v}\right) \underline{N}_1 \text{ (approx.)} \tag{39}$$

where M is the molecular weight of the solvent. The quantity in the parenthesis is evidently composed of constants which are characteristic of the solvent only, and are quite independent of the nature of the solute. This parenthesis is called the **molal boiling-point raising** for the solvent in question and is represented by the symbol, k_B. Equation (39) may, therefore, be written

$$\Delta t_B = k_B \underline{N}_1 \text{ (approx.)} \tag{40}$$

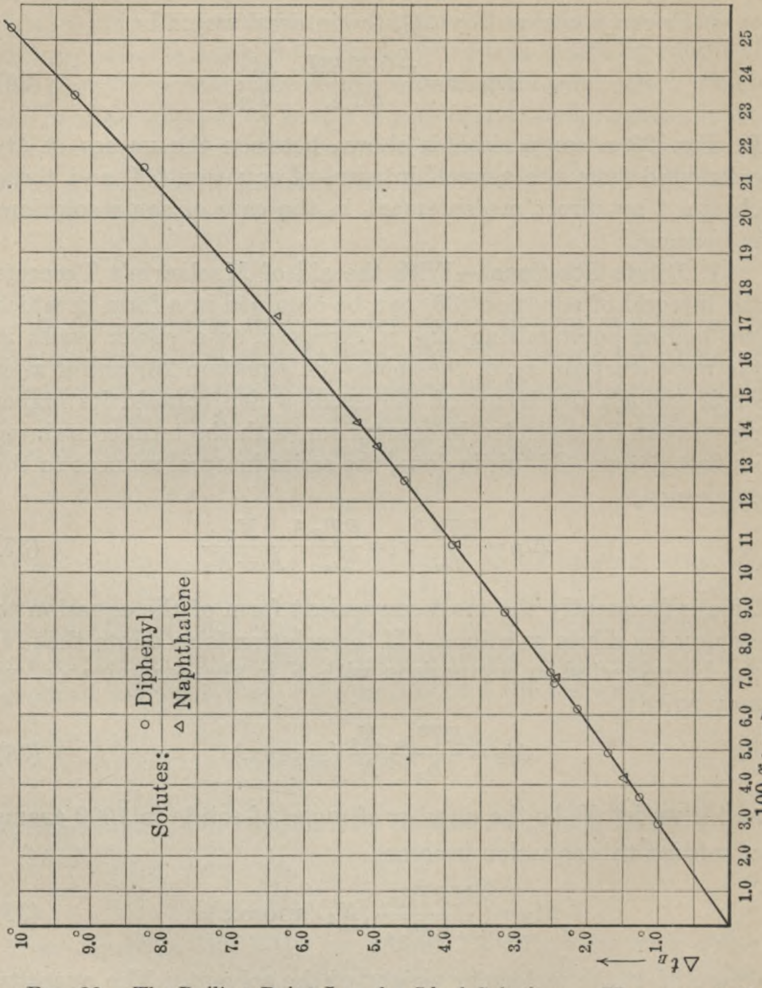

Fig. 22.—The Boiling Point Law for Ideal Solutions. The curve is the graph of the integral of the theoretical equation (35). The points represent observed values of Δt_B for solutions of naphthalene and of diphenyl in benzene. (Measurements by Washburn and Read, Jour. Amer. Chem. Soc., 1916.)

In using equations (36), (37), and (40) it should be remembered that the last two are only approximate ones and that except for very small values of Δt_B the three equations will give somewhat different results in a molecular weight calculation. In fact if either equation (37) or equation (40) is employed, due regard must be given to their limitations in comparison with the accuracy with which the value of Δt_B is measured and the desired accuracy in the molecular weight, for the case in question. For example, suppose that in order to determine the molecular weight of a substance in aqueous solution at 100°, the boiling-point raising for the solution is determined; and suppose that a solution containing 200 grams of the substance in 1000 grams of water gives $\Delta t_B = 1.000°$, accurate to 0.001°. If we calculate the molecular weight of the substance, we find 97.2 from equation (36), 98.6 from equation (37), and 102.2 from equation (39 or 40). If an accuracy of 1 per cent. is desired, it is evidently necessary to use equation (36) in calculating the value of M_1 in this instance. The use of equation (39) would give a result in error by 5 per cent.

If benzene were the solvent instead of water and if 38.73 grams of the substance dissolved in 1000 grams of benzene gave $\Delta t_B = 1.000°$ accurate to 0.001°, then the calculated values of M_1 would be 97.2 from equation (36), 98.5 from equation (37), and 101.6 from equation (39 or 40), very nearly the same values as in the case of water.

Problem 9a.—Perform the calculation indicated above for the same substance dissolved in alcohol, whose heat of vaporization at the boiling point, 79.8°, is 9990 cal. per mole.

In practice equation (40) is usually employed in molecular weight determinations by the boiling-point method and the constant, k_B, is determined by first finding the value of Δt_B for a solute of known molecular weight, and then solving equation (40) for k_B. This empirical value of k_B is then employed in calculating the value of M_1 for a solute of unknown molecular weight. This method of operation usually gives a more accurate value of M_1 than is the case when k_B is calculated from L_v, owing to a partial compensation of errors. In general, however, it is better and is always safer to employ equation (37) or better still equation (36) and to determine L_v, if necessary, by a boiling point determination with one or more solutes of known molecular weights.

Problem 10.—The heat of vaporization of benzene at its B. P., 80.2°, is 94.4 cal. per gram. Calculate the molal B. P. raising for benzene.

Problem 11.—A solution of 68 grams of a certain substance in 1000 grams of benzene boils 1.00° higher than pure benzene. What is the molecular weight of the substance?

Problem 12.—A solution of 66 grams of camphor, $C_{10}H_{16}O$, in 1000 grams of ethyl alcohol, C_2H_6O, boils at 79.31°. The pure alcohol boils at 78.81°. Calculate the latent heat of vaporization of alcohol at its boiling point. (Use equation (37)).

Problem 13.—The latent heat of vaporization of water at 100° is 540.7 cal. per gram. Approximately how many grams of dextrose, $C_6H_{12}O_6$, must be dissolved in 100 grams of water in order to raise its boiling point 0.1°?

THE FREEZING POINT AND SOLUBILITY LAWS

12. The General Freezing Point and Solubility Law.—If we put $T = T_F$ in equation (19) and then combine with equation (17, XII) so as to eliminate $d\Pi$, we have the desired relation, which is

$$dT_F = \frac{RT_F^2}{L_F}\frac{dx}{x} \tag{41}$$

From equation (11, XII) we have $T_F = T_{F_0} - \Delta t_F$ and $dT_F = -d(\Delta t_F)$ and hence

$$d(\Delta t_F) = \frac{-R(T_{F_0} - \Delta t_F)^2}{L_F}\, d\log_e x \tag{42}$$

It can be shown thermodynamically (XX, 10) that

$$L_F = L_{F_0} - \Delta C_P(\Delta t_F) \tag{43}$$

where L_{F_0} is the molal heat of fusion of the pure solvent at its freezing point and ΔC_P is the difference in the molal heat capacities of the solvent in the liquid and crystalline states, respectively. Combining this relation with equation (42) gives

$$d(\Delta t_F) = \frac{-R(T_{F_0} - \Delta t_F)^2}{L_{F_0} - \Delta C_P(\Delta t_F)}\, d\log_e x \tag{44}$$

and on integration we find

$$R\log_e x = \Delta C_P \log_e \frac{(T_{F_0} - \Delta t_F)}{T_{F_0}} - \frac{L_{F_0} - \Delta C_P(\Delta t_F)}{(T_{F_0} - \Delta t_F)} + \frac{L_{F_0}}{T_{F_0}} \tag{45}$$

as the general equation for the freezing point lowering of an ideal or a dilute solution. In this equation x is the mole fraction of the *solvent* in the solution and here, by the term "solvent," is meant that constituent whose pure crystals are in equilibrium with the solution. T_{F_0} is the absolute melting point of these crystals and L_{F_0} is their molal heat of fusion at $T°_{F_0}$. It may happen in a given case that ΔC_P is so small that it can be neglected, and then the above equation reduces to

$$R \log_e x = \frac{-L_{F_0}}{T_{F_0}} \frac{\Delta t_F}{T_F} \tag{46}$$

or

$$\log_{10} x = \frac{-0.4343 L_{F_0} \Delta t_F}{R T_{F_0} T_F} \tag{47}$$

Problem 14.—Pure naphthalene, $C_{10}H_8$, melts at 80.09°C. and its molal heat of fusion is 4560 calories. At what temperature will a solution composed of 76.9 grams of naphthalene and 61.6 grams of diphenyl, $C_{12}H_{10}$, be in equilibrium with crystals of pure naphthalene? (ΔC_P is negligible.)

Problem 15.—Pure diphenyl melts at 68.95°C. and its molal heat of fusion is 4020 calories. At what temperature will a solution composed of 46.1 grams of diphenyl and 89.6 grams of naphthalene be in equilibrium with crystals of pure diphenyl. (ΔC_P is not known.)

A solution made up of two components, A and B, has at least *two freezing points*, one being the temperature at which the solution is in equilibrium with pure crystals of component A, and the other the temperature at which it is in equilibrium with pure crystals of component B. The freezing-point diagram for such a system will therefore consist of two curves, one of which represents the temperatures at which solutions of varying composition are in equilibrium with crystals of component A, and the other of which represents temperatures at which the solutions are in equilibrium with crystals of component B. Such a diagram is shown in Fig. 23, mole fractions being plotted as abscissæ and freezing points as ordinates. The temperature at which these two curves intersect each other is called the **eutectic point** and is the temperature at which a solution having the composition shown by the abscissa of the point is in equilibrium with *both* crystalline phases at the same time. Evidently there is only one temperature and one composition of solution for which this condition can exist. For an ideal solution the two freezing point curves will be the graphs of equation (47) [or more accurately of equation (45)] for the two components, respectively, and by solving these equations simultaneously, the position of the eutectic point can be readily calculated. A comparison of the values thus calculated with values obtained by direct measurement for the systems, naphthalene-diphenyl, diphenyl-benzene, and naphthalene-benzene, is given in Table XVIII below and the complete freezing-point diagram for these three systems is shown in Fig. 24.

The curves shown in this figure are frequently called solubility curves as well as freezing point curves. The reason for this dual

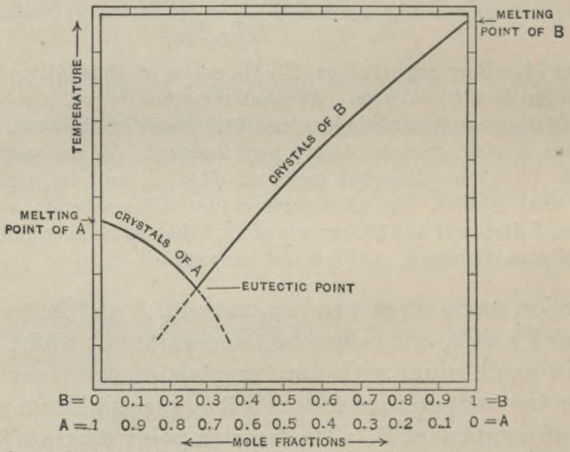

FIG. 23.—Typical Freezing-Point Diagram for a two Component System.

naming is the following: If we take any point, P, on the naphthalene curve (Fig. 24), the ordinate of this point represents the temperature at which a solution having the composition given by the abscissa will begin to deposit crystals of pure naphthalene when it is cooled down from some higher temperature. In other words it is the freezing point of the solution with respect to naphthalene. On the other hand, if we take a quantity of pure liquid diphenyl and shake it with an excess of naphthalene crystals at the temperature corresponding to the ordinate of the point, P, the naphthalene will "dissolve" in the diphenyl until the composition of the resulting solution reaches the value given by the abscissa of the point, P. The quantity of naphthalene which dissolves under these conditions is called the **solubility** of naphthalene in diphenyl at the temperature in question. Obviously the curve shows how this solubility varies with the temperature. Hence the name, "solubility curve." Solubility may be expressed in any one of the various ways in which composition of a solution is expressed, as explained in Section 5 of Chapter XI.

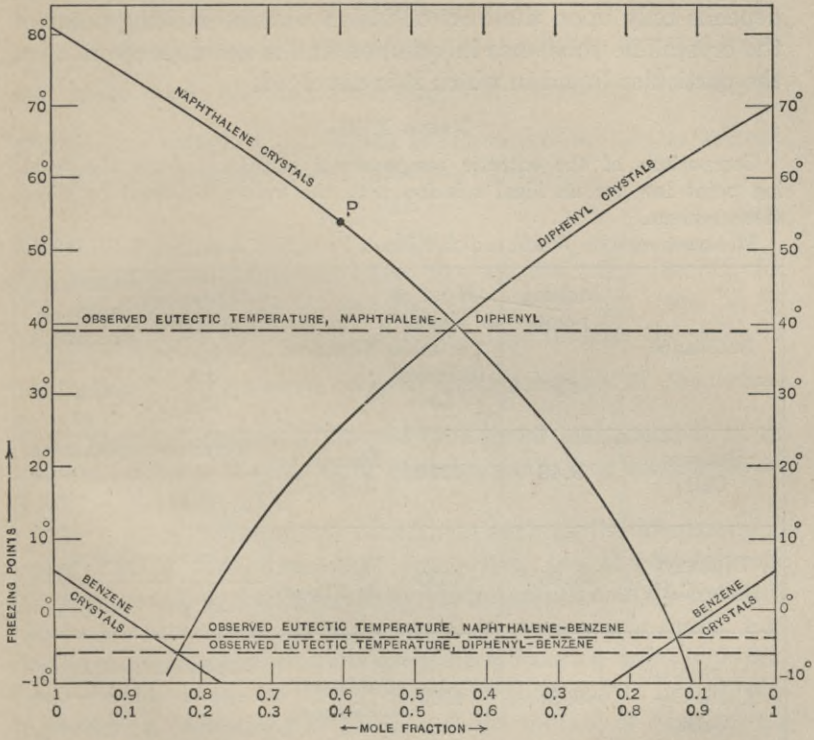

Fig. 24.—Freezing-Point—Solubility Diagram for the Systems, Naphthalene-diphenyl, Napthalene-benzene and Diphenyl-benzene. The curves are the graphs of the theoretical freezing point equation (47) and are named according to the substance present as the crystalline phase.

Problem 16.—Calculate the solubility of naphthalene in benzene at 0°C. The data necessary for the calculation are given in Table XVIII. Express the result as grams of naphthalene per hundred grams of solution. Calculate also the solubility of naphthalene in toluene at 25° in the same units.

This problem is given in order to emphasize the fact that, at any given temperature, the solubility (expressed as the molecular fraction of the molecular species in question) of any pure crystalline substance in a liquid with which it forms an ideal solution depends only upon the heat of fusion and the melting point of the crystalline substance in question and is not dependent upon the particular liquid in which it is dissolved.

TABLE XVIII

Comparison of the eutectic temperatures calculated from the freezing point law for an ideal solution with the values obtained by direct measurement.

Measurements by Washburn and Read, Proc. Nat. Acad. Sci. **1,** 191 (1915).

Substance	Melting point $t°_F$	Heat of fusion per mole (calories) L_F	Observer	Observed eutectic temperature $t°_E$	Calculated eutectic temperature (equation 47)
Benzene C_6H_6	5.48	2370	Demerliac J. Meyer	Benzene-naphthalene	
				−3.48	−3.56
Diphenyl $C_6H_5–C_6H_5$	68.95	4020	Washburn and Read	Benzene-diphenyl	
				−5.8	−6.1
Naphthalene $C_4H_4–C_2–C_4H_4$	80.09	4560	Alluard Pickering	Naphthalene-diphenyl	
				39.4	39.4

13. Freezing Points of Dilute Solutions.—When the mole fraction of the solute is small we may integrate equation (44) by means of Maclaurin's Theorem in exactly the same way as in the case of the corresponding boiling point equation and obtain the similar equations,

$$\Delta t_F = \frac{RT_{F_0}^2}{L_{F_0}} x_1 = \frac{RT_{F_0}^2}{L_{F_0}} \frac{N_1}{N+N_1} \text{ (approx.)} \tag{48}$$

$$\Delta t_F = \frac{RT_{F_0}^2}{L_{F_0}} \frac{N_1}{N} \text{ (approx.)} \tag{49}$$

$$\Delta t_F = \frac{MRT_{F_0}^2}{1000\,L_{F_0}} \underline{N}_1 \text{ (approx.)} \tag{50}$$

and

$$\Delta t_F = k_F \underline{N}_1 \tag{51}$$

which correspond exactly to the boiling point equations (37), (38), (39) and (40) and are applicable under analogous conditions. The constant, k_F, is called the **molal freezing point lowering** for the solvent in question. Equations (49–51) are usually known as the Raoult–Van't Hoff equations.

In words equation (51) states that as the solution becomes more and more dilute the molal freezing point lowering, $\frac{\Delta t_F}{\underline{N}_1}$, should approach a constant, k_F, which is characteristic of the solvent and which can be calculated from the relation,

$$k_F = \frac{MRT_{F_0}^2}{1000\, L_{F_0}} \tag{52}$$

For aqueous solutions we have, $M=18$, $R=1.985$ (see II, 7), $T_{F_0}=0°+273.1°, =273.1°$, and $L_{F_0}=18\times 79.60$ cal. (see X, 6) and hence $k_F=1.86°$. Bedford[4] determined directly the value of the ratio, $\frac{\Delta t_F}{\underline{N}_1}$, for a series of cane sugar solutions of concentrations ranging between 0.005 and 0.04 molal and found it to be constant within the limits of experimental error and equal to 1.86°. (See Fig. 27.)

For aqueous solutions of substances such as the alcohols and sugars which resemble water somewhat, the thermodynamic environment may be expected to remain approximately constant up to concentrations as high as one or two weight-molal, and for such high concentrations the general freezing point equation (45) should always be employed rather than any of its approximate forms (equations 48 to 52). With the aid of Maclaurin's Theorem this general equation can be put in the form of a series. If this is done and the numerical values of the constants for water are substituted, the two expressions,

$$x_1 = 0.009690(\Delta t_F - 0.00425\Delta t^2{}_F) \tag{53}$$

$$\Delta t_F = 103.20(x_1 + 0.428x_1^2) \tag{54}$$

are obtained. For ideal solutions in which water is the solvent these expressions are accurate to 0.001° provided Δt_F is not greater than 7°.

In Fig. 25 is shown the graph of these equations together with the observed values of Δt_F for methyl and ethyl alcohols and for cane sugar. The agreement in the case of the alcohols is very good but the observed points for cane sugar fall below the theoretical curve. If, however, we assume that cane sugar exists in solution in the form of the hydrate, $C_{12}H_{22}O_{11}\cdot 6H_2O$, and calculate the mole fractions of this hydrate by means of equation (23) the points thus obtained (dotted circles in the figure) fall

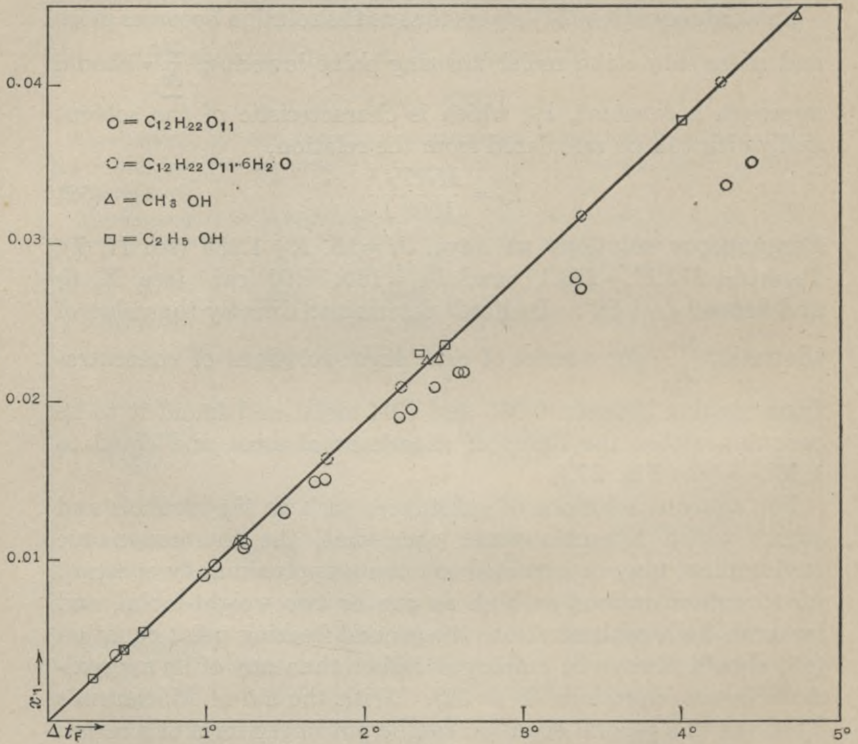

FIG. 25.—The Freezing Point Law for Aqueous Solutions. The curve is the graph of the theoretical equation, (52). The points represent observed values of Δt_F for the substances indicated, [Technology Quarterly, **21,** 376 (1908)].

exactly on the theoretical curve, thus confirming the osmotic pressure results for these solutions (see Table XVII). The results for the alcohols indicate that they are either not hydrated in aqueous solution or else that the hydrate is one containing not more than one molecule of water. The data do not warrant a more exact conclusion than this owing to the assumption of 18 as the molecular weight of water.

Problem 17.—Calculate the freezing point of a weight molal solution of chloral hydrate, $CCl_3COH \cdot H_2O$, in water.

Problem 18.—From the data given in Table XVIII calculate the volume of methane, CH_4 (measured under standard conditions) which must be dissolved in 1000 grams of benzene in order to lower its freezing point 0.6°.

14. The Solubility Law for Dilute Solutions.—In the case of dilute solutions the term *freezing-point curve* is usually restricted to the curve representing the temperatures at which solutions of varying composition are in equilibrium with the pure crystalline *solvent;* while the term, *solubility curve,* is applied only to the curve which represents the compositions of solutions which at different temperatures are in equilibrium with the pure crystals of the *solute.* In the former case the heat of fusion of the substance present in the crystalline state (*i.e.*, the solvent) is identical with its heat of solution in the "dilute solution," for by definition (XIII, 3) this solution has the same thermodynamic environment as that which prevails in the pure liquid solvent. In the latter case, however, this condition is not true except for ideal solutions, for the thermodynamic environment in a dilute solution is in general very different from that which prevails in the pure liquid solute. Equation (41) applies to both cases but in the latter case in place of L_F, the molal heat of fusion of the solute crystals, we must write $L_{Sl.}$, the molal heat of solution of these crystals in enough solvent to form a "dilute solution." Equation (41) would, therefore, read

$$dT = \frac{RT}{L_{Sl.}} \frac{dx_1}{x_1} \tag{55}$$

or

$$\left(\frac{\partial \log_e x_1}{\partial T}\right)_P = \frac{L_{Sl.}}{RT} \tag{56}$$

where T is the temperature at which the crystals of the solute are in equilibrium with a dilute solution in which the mole fraction of the solute is x_1 and $L_{Sl.}$ is the heat *absorbed* when one mole of the solute crystals is dissolved in enough of the solvent to form a "dilute solution."

If we assume $L_{Sl.}$ constant, the integral of this equation is,

$$\log_{10} \frac{x'_1}{x_1} = \frac{0.4343 L_{Sl.}}{R} \left(\frac{1}{T} - \frac{1}{T'}\right) \tag{57}$$

or, since x_1 is small,

$$\log_{10}\frac{S'}{S}=\frac{0.4343L_{sl.}}{R}\left(\frac{1}{T}-\frac{1}{T'}\right)\text{ (approx.)}\qquad(58)$$

where S is the solubility of the solute (expressed in any desired units) at the temperature, T, and S' is its solubility at the temperature, T'.

Problem 19.—The solubility of iodine, I_2, in water is 0.001341 mole per liter at 25° and 0.004160 mole per liter at 60°. What is the molal heat of solution of iodine within this temperature range? What is the solubility of iodine at 40°?

15. The Application of the Solution Laws to the Interpretation of Processes Occurring within the Solution. (*a*) **The Distribution Laws.**—Since all of the solution laws discussed in this chapter involve the molecular weight of at least one of the constituents, they are made the basis for the determination of molecular weights in solution. In employing the laws for this purpose the assumptions implied in their derivation and the exact significance of the quantities which they involve must be kept clearly in mind. Thus in using any one of the distribution laws it must always be remembered that these laws are derived only for the distribution of *a given molecular species* and it is the mole fraction or concentration of the molecular species in question which belongs in the equation of the law and *not the total mole fraction* of the solute, if the latter happens to be made up of more than one molecular species. For example, when acetic acid is in distribution equilibrium between water and benzene there are present in the system the two molecular species, CH_3COOH and $(CH_3COOH)_2$ and each species will distribute itself between the two phases in accordance with the distribution law and will have its own characteristic distribution constant. But if we were to substitute in the distribution law (equation (15)) the mole fraction of acetic acid in each phase, arbitrarily calculated on the assumption that it exists only as CH_3COOH-molecules in both phases, we would find that the "distribution constant" thus calculated was far from being constant. In other words, the law would apparently not be obeyed. The failure of the law in such a case would be only an apparent one, however, owing to the fact that we have through ignorance not substituted the proper values in the equation. We have an example of a deviation of this character in Table XV where the values of the calculated distribution constant are seen to decrease slightly but steadily as C_w increases. It is known from independent evidence, however, that the mercuric bromide is partially dissociated in the water layer and that the degree of this dissociation increases with the dilution of this layer, that is, it increases as C_w decreases. The result is that the true value of C_w for the $HgBr_2$-molecules is in reality less than the total concentration of mercuric bromide in the water layer by an amount which is proportionally greater the smaller C_w and this is sufficient to account for the slight apparent deviation from the law shown in Table XV.

(*b*) **The Osmotic, Freezing Point, and Boiling Point Laws.**—With reference to those solution laws which involve one of the colligative properties of the "solvent" (the freezing point, boiling point, and osmotic pressure laws) it should be remembered that in the equations of these laws (equations 25 to 29, 37 to 40, and 48 to 51)) the quantities x_1, $\underline{N}_1$, and C_1, referring to the amount of the solute molecules, signify (as is evident from the derivation of these equations) the *total* mole fraction or concentration of *all* species of solute molecules in the solution and not the value for some one of these molecular species as was the case for the distribution laws. For example, if one gram molecular weight of acetic acid (CH_3COOH) were dissolved in 1000 grams of benzene, the quantity $\underline{N}_1$ in equation (51) would be unity provided all of the acetic acid when in solution existed in the form of CH_3COOH-molecules. If, however, half of it were in the form of $(CH_3COOH)_2$-molecules, the solution would actually contain 0.25 gram molecular weight of $(CH_3COOH)_2$-molecules and 0.5 gram molecular weight of CH_3COOH-molecules or altogether 0.75 gram molecular weight of solute molecules and this is the value for $\underline{N}_1$ which would then belong in equation (51). Since the molecular condition of the acetic acid in the benzene is not known in advance we could evidently obtain some light upon this question by measuring the freezing point lowering produced by known quantities of acetic acid and then calculating the value of $\underline{N}_1$ and hence the molecular weight by means of equation (51).

(*c*) **Molecular Weights in Solution.**—By the investigation of the behavior of solutions with reference to the solution laws the following facts regarding the molecular weights of substances in solution have been ascertained: (1) Almost all substances (except salts, acids and bases) when dissolved in water, alcohol, ether, acetic acid, or in general any solvent containing oxygen in its molecule have either the same molecular weight as they have in the gaseous state or a greater molecular weight due to the fact that they have united with some of the solvent to form a *solvate.* (2) The same statement is true of almost all organic substances (except those which contain an hydroxyl group) when dissolved in any solvent. (3) Compounds containing hydroxyl (alcohols, acids) when dissolved in organic liquids whose molecules contain no oxygen (hydrocarbons, halogen and sulphur compounds, etc.) are *associated* (III, 5), at least partially, in the solution. (4) Salts, acids, and bases in many solvents, especially in water, have apparently molecular weights smaller than those corresponding to their formulas, that is, they are *dissociated,* at least partially, into smaller molecules. This dissociation, known as electrolytic dissociation (I, 2g), and the properties to which it gives rise will form the topic of the next division of our subject.

(*d*) **The Interpretation of Experimental Data.**—Probably the greatest source of uncertainty in the use of the solution laws for interpreting the processes occurring within a solution lies in the difficulty of distinguishing between apparent divergencies from the laws, such as those described above, and real divergencies resulting from the fact that the thermodynamic environment within the solution is not constant. Frequently divergencies from both sources are present simultaneously and it is necessary to use great caution in drawing conclusions in such instances and to confirm any conclusions drawn, by evidence from sources of an entirely different character. The interpretation of scientific data with the help of a set of derived relationships such as the laws of solutions cannot be intelligently made unless the derivation of the laws and all of the assumptions involved therein are clearly understood by the one who is attempting to employ them. The literature of chemistry unfortunately abounds with examples illustrating the truth of this maxim and it is for this reason that so much space and attention have been devoted to the derivation of the solution laws in this chapter. It may be well to mention also at this point a not infrequent error in logic made by beginners.

Suppose, for example, that postulating A and B as true we can demonstrate by purely logical reasoning the truth of C as a necessary consequence. Evidently then if we are able to prove by experiment that A and B are true, we at the same time establish the truth of C. Suppose, however, that we are able to show by direct experiment that C is true. It by no means follows from this that A and B are true, however. Before we are justified in drawing this conclusion we must first demonstrate that A and B are the only possible or reasonable assumptions from which the truth of C can be shown to follow. In other words if a derived relation, such as one of the solution laws for example, is found experimentally to hold true for a given case, it by no means necessarily follows that the assumptions on the basis of which the relationship was derived also hold true for that case.

Problem 20.—Show that equations (28, 29, 38, 39, 49 and 50) are independent of the molecular weight of the solvent and that hence no information concerning the molecular weight of a solvent can be obtained from freezing point, boiling point or osmotic pressure measurements of dilute solutions.

Problem 21.—A certain molecular species in dilute solution is in distribution equilibrium between two solvents. If equation (9) holds true for the vapor of this species above the two solvents show that equation (16), $\frac{\underline{N}_1}{\underline{N}_2} = \text{const.}$, must also hold true. If equation (9) is not true but if instead the relations, $p_1 = k_1\underline{N}_1 + k'_1\underline{N}_1^2$ and $p_2 = k_2\underline{N}_2 + k'_2\underline{N}_2^2$, hold true for the vapor pressures of the solute from the two liquid phases respectively, show that the relation $\frac{\underline{N}_1}{\underline{N}_2} = \text{const.}$, will still hold true within 0.1 per cent. for all cases in which $\left(\frac{k'_1}{k_1} - \frac{k'_2\,k_1}{k_2^2}\right)\underline{N}_1 \not> 0.001$.

Problem 22.—Two liquids, A and B, when shaken together dissolve in each other forming two nonmiscible solutions. Show with the aid of thermodynamics (X, 10) that neither substance can obey the vapor pressure law of Ideal Solutions (equation 3) in *both* solutions; in other words, that two liquids cannot form an Ideal Solution with each other unless they are miscible in all proportions.

Concentrated Solutions in General

16. Solutions of Variable Thermodynamic Environment.—Whenever the thermodynamic environment in a solution varies with its composition, the laws developed in the preceding sections of this chapter are no longer applicable. The magnitude and direction of the departure from these limiting laws in any given case depends upon the natures of the constituents of the solution and for this reason a satisfactory quantitative theory for solutions in general has not yet been developed (cf. XII, 9) and owing to the nature of the problem there seems to be no immediate likelihood that such a theory will be formulated. In working, therefore, with solutions in which the thermodynamic environment cannot be regarded as constant (and this is the case with most solutions), each solution must be treated as a problem by itself and the quantitative relation connecting some one of its colligative properties (the vapor pressure, for example) with the composition must be determined by direct experiment. The other relations can then be derived with the aid of thermodynamics. Although a quantitative theory for solutions in general is lacking, there are a few useful principles of a qualitative nature which are applicable to all solutions and which are of considerable practical assistance in the intelligent carrying out of some of the operations to which solutions are subjected in the laboratory and the industries. We shall discuss two of these briefly.

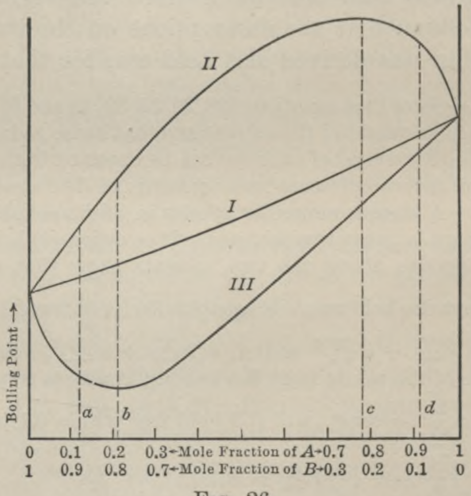

FIG. 26.

17. The Theory of Distillation.—The boiling point-composition curves for homogenous liquid mixtures may be conveniently divided into three types which are illustrated in Fig. 26. In type I the boiling point rises continuously from the boiling point of one pure constituent to the boiling point of the other. The curve for ideal solutions is of this type. Type II exhibits a maximum and type III a minimum boiling point at a certain composition.

If a homogeneous liquid mixture of two constituents be subjected to fractional distillation at constant pressure, it is obvious that as the distillation progresses the more volatile portion of the mixture will collect in the distillate while the less volatile portion will remain in the residue. Or in other words *the composition of the distillate, continuously approaches that of the liquid having the minimum boiling point, while the composition of the residue continuously approaches that of the liquid having the maximum boiling point.* This is the principle at the basis of the theory of fractional distillation. Its application to specific cases will be understood by the solution of the following problems.

Problem 23.—Each of the four solutions having the compositions indicated by the dotted lines in Fig. 26 is separated as completely as possible into two portions by fractional distillation at constant pressure. What will be the composition of each portion assuming that the boiling point curve is (1) of type I, (2) of type II and (3) of type III?

Problem 24.—In making up a standard solution of hydrochloric acid it is sometimes convenient to remember that if *any* hydrochloric solution of unknown strength be taken and boiled in the open air (760 mm.) for a sufficient length of time, it will attain the composition 20.2 per cent. HCl, boiling at 110°, and may then be diluted to the desired strength. Draw a diagram showing the character of the boiling point curve for HCl solutions in water. See Table XII for the additional datum required.

18. Distillation of Nonmiscible Liquids.—When liquids which are mutually insoluble (or practically so) in one another are heated together the mixture will boil when the sum of the separate vapor pressures of the components reaches a value equal to the external pressure on the mixture. This temperature can be readily determined if the vapor pressure curves of the component liquids are known. It will necessarily be lower than any of the boiling points of the components and may be far lower than some of them. This makes it possible to effect the distillation of a high boiling liquid at a temperature much below its boiling point without having recourse to vacuum distillation and is the principle at the basis of the process of distillation by steam which is frequently employed in the purification by distillation of such liquids as aniline, nitrobenzene, and oils which are insoluble in water. The composition of the distillate from such a distillation can be calculated by means of Dalton's law of partial pressures (II, 6) if the vapor pressures of the pure components at the boiling point of the mixture are known.

Problem 25.—A current of steam is passed at atmospheric pressure through a mixture of water and chlorbenzene (C_6H_5Cl). From the data recorded in the Landolt-Börnstein tables, determine the boiling point of the mixture and the per cent. by weight of chlorbenzene in the distillate.

19. The Theory of Fractional Crystallization.—When a solution is fractionated by distillation, the theory of the process is much simplified by the fact that only one gaseous phase is possible (I, 8) in the system. When the fractionation is carried out by crystallization, however, our problem may become a very complicated one owing to the large number of different crystal phases which are possible. The general principle underlying the theory of fractional crystallization may be stated as follows: *When a homogeneous liquid mixture of two constituents is subjected to fractional crystallization the composition of the mother liquor continuously approaches the liquid having the lowest crystallization temperature.* This liquid is usually a eutectic mixture of some kind although it may be one of the pure constituents. The crystals which separate during the fractionation may be either (1) one of the pure constituents, (2) a compound between the two, (3) mixed crystals containing both constituents, or (4) mixed crystals containing one of the constituents and a compound between the two. We shall not here enter upon the detailed discussion of these special cases as they are more conveniently taken up in connection with the discussion of the Phase Rule and its applications (XXIV, 12).

REVIEW PROBLEMS

Problem 26.—The vapor pressure of ether ($C_4H_{10}O$) at 13° is 33.18 cm. This is lowered by 0.80 cm. by dissolving something in the ether. The specific gravity of ether is 0.721. Calculate the osmotic pressure in atmospheres of this solution. (See prob. 6, Chap. XII.)

Problem 27.—The value 0.0198 for the relative vapor pressure lowering of a weight molal solution of cane sugar in water at 25° has been found by direct experiment. Calculate the osmotic pressure of the solution. (Answer: 27.1 atm. Compare with the observed osmotic pressure given in Table XVI.) (See prob. 6, Chap. XII.)

Problem 28.—At 30° the vapor pressure of pure ether ($C_4H_{10}O$) is 64 cm. and that of pure water is 3.1 cm. When the two liquids are shaken together at 30°, 1 gram of water is dissolved by 73 grams of ether and 1 gram of ether by 18.8 grams of water. Calculate the total vapor pressure above the mixture.

Problem 29.—Five liters of air measured at 20° and 1 atm. are passed through a saturater containing liquid ether at 20° and the air saturated with ether vapor issues from the saturater under a total pressure of 1 atmosphere. The vapor pressure of ether at 20° is 44.2 cm. How many grams of ether will be vaporized?

Problem 30.—In problem 9a if the CCl_4 solution is shaken with 9 successive portions of water of 3 liters each, how many grams of iodine will be left in the CCl_4 layer?

Problem 31.—The latent heat of vaporization of cyclohexane is 89 cal. per gram at its boiling point, 81.5°. How many grams of anthracene ($C_{14}H_{10}$) must be dissolved in 200 grams of cyclohexane in order to raise its boiling point 0.1°?

Problem 32.—At what temperature will a solution of 1 gram of toluene ($C_6H_5CH_3$) in 1000 grams of benzene be in equilibrium with crystals of benzene? See Table XVIII for additional data.

Problem 33.—The freezing point of water saturated with pure ether ($C_4H_{10}O$) is $-3.84°$, and that of a water solution which is in equilibrium with an ether solution containing in 156 grams of solution, 8.0 grams of a hydrocarbon (having 6.25 per cent. of hydrogen) is $-3.72°$. Derive an expression by means of which the molecular weight of the hydrocarbon may be approximately computed from these data alone. State clearly the assumptions made in your derivation. What is the empirical formula of the hydrocarbon?

Problem 34.—The freezing point of an aqueous solution of a non-volatile non-electrolyte is $-0.125°$. What will be its boiling point at 760 mm.? What at 750 mm.?

Problem 35.—When benzene is shaken with *successive* portions of a 0.1 weight molal aqueous solution of a non-electrolyte until distribution equilibrium is attained, the benzene solution thus formed is found to have a freezing point lowering of 0.253°. If 2 liters of a 0.05 weight molal aqueous solution of the non-electrolyte be shaken with 4 liters of benzene until equilibrium is reached, what will be the freezing point of the aqueous solution remaining?

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CHAPTER XV

THE COLLIGATIVE PROPERTIES OF SOLUTIONS OF ELECTROLYTES

1. The Molal Freezing Point Lowering.—We have already learned (XIV, 13) that the molal freezing point lowering$(\frac{\Delta t_F}{\underline{N}_1} = k_F)$ for any solvent should theoretically reach a constant limiting value in dilute solution and that for aqueous solutions this limiting value should be 1.86°. In the case of all aqueous solutions which do not conduct electricity this theoretical conclusion has been completely and quantitatively confirmed by direct experiment, not a single exception to it having ever been discovered. But in the case of all aqueous solutions which do conduct electricity this conclusion is apparently never confirmed, since such solutions without exception give decidedly larger values than 1.86° for the molal freezing point lowering at infinite dilution. These facts are illustrated graphically in Fig. 27. In the case of sugar solutions the value of k_F is constant and equal to 1.86° for all values of $\underline{N}_1$ below 0.01. With salts of the types of KCl and $MgSO_4$ the values of k_F are all larger than those for sugar and gradually approach the limiting value, 3.72° (=2×1.86°) as $\underline{N}_1$ decreases. The values for $BaCl_2$ are still larger and approach a limit which is evidently close to 5.58° (=3×1.86°) while in the case of K_3FeCy_6 the limiting value must evidently be close to 7.44° (=4×1.86°). These figures are typical of those obtained with all solutions of substances which conduct electricity. The limiting value of k_F instead of being 1.86° is invariably some small exact multiple of this number. In other words the freezing point lowering is always much larger than the value corresponding to the molecular weight of the solute.

2. The Other Colligative Properties.—From the results obtained for the freezing point lowerings of aqueous solutions of substances which conduct electricity it necessarily follows (see XII, 8) that the other colligative properties of these solutions, the osmotic pressure, the boiling point raising and the vapor pressure lowering, must likewise be abnormally large and this is completely confirmed by the results of experiment. Thus the osmotic pressure of a 0.5 weight molal solution of KCl at 25° has been found[1] to be larger than 20 atmospheres and its relative vapor pressure lowering is 0.014. The corresponding values for substances which do not conduct electricity are 12 atmospheres and 0.009.

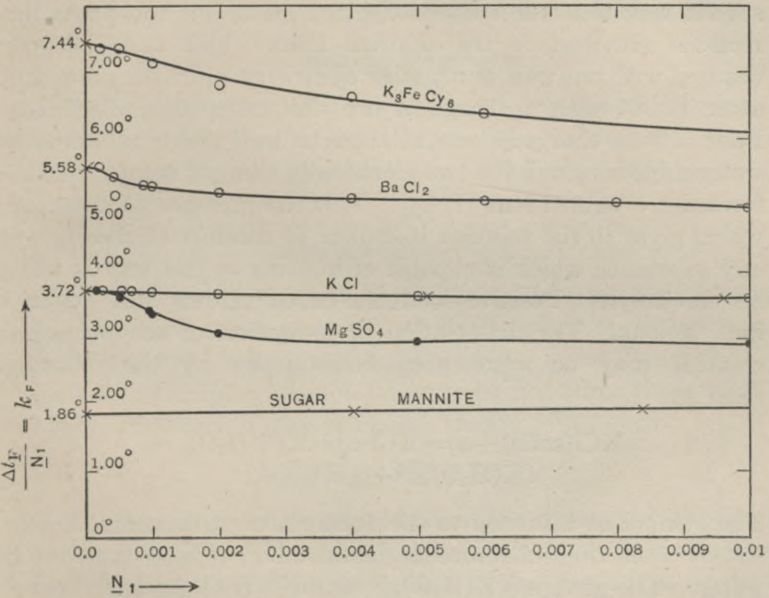

FIG. 27.—Variation of molal freezing point lowering with concentration for aqueous solutions. The centers of the circles represent Bedford's measurements. The crosses are measurements by Adams (Jour. Amer. Chem. Soc., Mar., 1915). Bedford has not published his individual values for sugar, merely stating that they were constant for the above range. The crosses on the lower curve are Adams' values for mannite.

These facts and a great many others concerning the behavior of solutions which conduct electricity find their only successful interpretation in the Ionic Theory which was first proposed by

Arrhenius[a] in 1887. In the following pages the Ionic Theory will, therefore, be employed as the framework for the systematic development and presentation of our present knowledge of solutions of electrolytes.

3. The Ionic Theory. (*a*) **Electrolytic Ionization.**—According to the Ionic Theory when a salt, such as KCl for example, is dissolved in water, part of its molecules split up or dissociate in such a way that the valence electron (I, 2*g*) of the potassium remains attached to the chlorine atom which thus becomes charged with one unit of negative electricity while the potassium atom is left with a charge of one unit of positive electricity. Each of these charged atoms attaches to itself a certain number of water molecules and the two electrically charged complexes thus formed are termed **ions** (I, 2*g*). It is the presence of these ions which gives to the solution its power to conduct electricity and any substance which is capable of ionizing in this way is called an **electrolyte.** Positive ions are called **cations** and negative ions, **anions.** The dissociation or ionization of the potassium chloride may be represented symbolically by the following reaction:

$$\mathrm{KCl(solid)} + aq = \mathrm{KCl}\cdot aq = \mathrm{KCl(H_2O)}_p = \\ [\mathrm{K(H_2O)}_m]^+ + [\mathrm{Cl(H_2O)}_n]^- \qquad (1)$$

The symbol *aq* attached to the formula of a substance means simply that the substance is dissolved in a large amount of water. The groups $[(\mathrm{K(H_2O)}_m]^+$ and $[\mathrm{Cl(H_2O)}_n]^-$ are the two ions. The numerical values of m and n in these expressions are not known and it is usually customary to omit the attached water in writing the symbol for an ion. Thus the ionization reaction for KCl is usually abbreviated thus,

$$\mathrm{KCl} \rightleftarrows \mathrm{K^+} + \mathrm{Cl^-} \qquad (2)$$

The character, $\rightleftarrows$, indicates that there is a chemical equilibrium (I, 9) between the two ions and the un-ionized molecules, that is, the ionization of the KCl at finite concentrations is not complete, a certain number of un-ionized molecules always being present in the solution. As the solution is diluted more

[a] Svante August Arrhenius, (1859-). Director of the Laboratory of Physical Chemistry of the Nobel Institute in Stockholm.

and more, however, the number of un-ionized molecules continually decreases and finally at infinite dilution the KCl is completely ionized and for every mole of KCl which was originally dissolved there are actually present in the solution *two moles* of solute molecules, the two ions. The molal freezing point lowering of this solution should, therefore, be just twice as great as the value for a substance like sugar whose molecules do not break up in solution. The same is true of $MgSO_4$ which ionizes thus,

$$MgSO_4 = Mg^{++} + SO_4^{--} \tag{3}$$

the two ions in this instance being each charged with *two* units of electricity, since the sulphate ion retains *both* of the valence electrons of the magnesium atom. Barium chloride ionizes thus

$$BaCl_2 = Ba^{++} + 2Cl^- \tag{4}$$

giving *one* doubly charged barium ion and *two* singly charged chloride ions. One molecule of $BaCl_2$ when it ionizes gives, therefore, *three* solute molecules and its molal freezing point lowering at infinite dilution ought to be just three times 1.86° or 5.58°. Similarly K_3FeCy_6 ionizes thus

$$K_3FeCy_6 = 3K^+ + FeCy_6^{---} \tag{5}$$

to give *three* singly charged potassium ions and *one* triply charged ferricyanide ion. Its molal freezing point lowering at infinite dilution ought therefore according to the Ionic Theory to be exactly four times 1.86° or 7.44°; all of which accords completely with the experimental results displayed in Fig. 27.

(*b*) **Nomenclature and Types of Electrolytes.**—Ions are named from the atom or group of which they are formed. Thus all potassium salts give potassium ion K^+ when they ionize, all ammonium salts give ammonium ion NH_4^+, all chlorides including hydrochloric acid give chloride ion Cl^-, all acids give hydrogen ion H^+, and all hydroxides give hydroxyl ion OH^-.

Electrolytes are classified according to the character of their ions as uni-univalent (KCl, HCl, NH_4NO_3), which give two singly charged ions; uni-bivalent ($BaCl_2$, H_2SO_4, $Ca(OH)_2$), which give two singly charged and one doubly charged ion; bi-bivalent ($MgSO_4$, BaC_2O_4), which give two doubly charged ions;

uni-trivalent ($FeCl_3$, Na_3PO_4, K_3FeCy_6), which give three singly charged and one triply charged ion; bi-trivalent ($Fe_2(SO_4)_3$, $Ba_3(PO_4)_2$) which give two triply charged and three doubly charged ions; tri-trivalent ($FePO_4$), which give two triply charged ions; etc.

Problem 1.—Write the ionization reactions of the above electrolytes. Give also examples of still higher types and write their ionization reactions. Name the ions in each instance.

4. Degree of Ionization.—If $\underline{N}_1$ formula weights of an electrolyte be dissolved in 1000 grams of water, a certain fraction of its molecules will ionize and this fraction is called the **degree of ionization,** α, of the electrolyte at this concentration. For a uni-univalent electrolyte the concentration of *each* species of ion in the solution will evidently be $\alpha\underline{N}_1$ and that of the un-ionized molecules $(1-\alpha)\underline{N}_1$, moles per 1000 grams of water. The *total concentration* of solute molecules in this solution will, therefore, amount to $2\alpha\underline{N}_1+(1-\alpha)\underline{N}_1$ or $(1+\alpha)\underline{N}_1$ moles per 1000 grams of water. In other words the number of *formula weights* of a uni-univalent electrolyte dissolved in a given quantity of water must be multiplied by $(1+\alpha)$ in order to obtain the *actual number of moles of solute* in the resulting solution.

In order to calculate the value of α for a given case we might multiply the quantity $\underline{N}_1$ in any one of the solution laws by $1+\alpha$ and solve the resulting equation for α. In this way we would, for example, obtain from the freezing-point law for aqueous solutions (equation 53, XIV) the relation

$$x_1=\frac{(1+\alpha)\underline{N}_1}{\frac{1000}{18}+(1+\alpha)\underline{N}_1}=0.009690\ (\Delta t_F-0.00425\ \Delta t_F^2) \tag{6}$$

from which we could evidently calculate a value for α from the observed freezing point lowering of the solution. The calculation of degree of ionization in this manner, however, assumes (1) that the solute is not hydrated in solution, and (2) that the thermodynamic environment in the solution is the same as that which prevails in pure water, for these are the assumptions upon which equation (53, XIV) was derived. Neither of these assumptions is true, however. The ions and in many cases the un-ionized molecules are known to be hydrated in solution and the whole behavior of solutions of electrolytes indicates that the thermodynamic environment even at fairly small ion concentrations (Cf. XIII, 3) may be quite appreciably different from that which prevails in pure water.

The use in this manner, of any of the Laws of Solutions of Constant Thermodynamic Environment in order to calculate the degree of ionization of an electrolyte has, therefore, no theoretical justification.[2] These laws have nevertheless been extensively employed for this purpose and when the values of α calculated in this way are compared with those obtained by the conductivity method (XVII, 2b) the agreement in many cases is so close as to make it probable that the two erroneous assumptions mentioned above happen to produce errors which are opposite in direction and which, therefore, partially compensate each other. Noyes[a] and Falk[b] who have examined a large number of electrolytes in this way[3] conclude that the degree of ionization of uni-univalent strong electrolytes in aqueous solution at concentrations not exceeding 0.1 molal can as a matter of fact be calculated from the freezing point lowering of the solution with an accuracy of from 1 to 4 per cent. *in most cases.* (Cf. Table XIV and XVII, 4.) We may, therefore, employ the solution laws in this way in order to compute *approximate* values for the degree of ionization of uni-univalent strong electrolytes, remembering that in so employing them we are treating them merely as empirical equations. For this purpose equation (6) may be rearranged algebraically into the more convenient form,

$$(1+\alpha)\underline{N}_1=\frac{\Delta t_F}{1.858}(1+0.0055\Delta t_F) \tag{7}$$

Problem 2.—The degrees of ionization of KCl, $CsNO_3$, and LiCl in 0.1 weight formal solution at 0° as measured by the conductance method are 0.88, 0.81, and 0.86 respectively. Calculate approximate values for the freezing points of these solutions. (Observed values are $-0.345°$, $-0.325°$, and $-0.351°$ respectively.)

Problem 3.—The freezing point of a 0.1 weight formal solution of $NaBrO_3$ is $-0.342°$. Calculate an approximate value for α.

[a] Arthur Amos Noyes, (1866–). Professor of Theoretical Chemistry and Director of the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology.

[b] Kaufmann George Falk, (1880–). Physical Chemist for the Harriman Research Laboratory, Roosevelt Hospital, New York.

Problem 4.—By direct measurement it has been found that at 25° a 0.5 weight formal solution of KCl has the same vapor pressure as a 0.91 weight formal solution of mannite ($C_6H_{14}O_6$) which is a non-electrolyte. From these two data estimate *approximately* the extent to which the KCl is ionized in the solution.

Electrolytes which are ionized to a large degree (50 per cent. or more in 0.1 normal solution) are called **"strong electrolytes."** They include nearly *all salts* and all of the so-called *strong acids and alkalies.* Electrolytes which are only slightly ionized are called **"weak electrolytes."**

5. Complex Formation in Solution.—Many electrolytes in solution possess the property of uniting with other electrolytes or with non-electrolytes to form complex compounds which ionize giving complex ions. Thus when KCN is added to a solution of $AgNO_3$ a reaction occurs which may be expressed stoichiometrically as follows:

$$2KCN + AgNO_3 = KNO_3 + KAg(CN)_2 \qquad (8)$$

The complex salt $KAg(CN)_2$ ionizes thus

$$KAg(CN)_2 = K^+ + Ag(CN)_2^- \qquad (9)$$

giving the very stable complex ion, $Ag(CN)_2^-$

Problem 5.—The freezing point of a 0.1 weight formal solution of KNO_3 is −0.33°. In an amount of this containing 1000 grams of water, 0.1 formula weight of NH_3 is dissolved and the freezing point then drops to −0.51°. A second 0.1 formula weight of NH_3 depresses it to −0.69° and a third to −0.9°. If the same experiments be carried out with 0.1 weight formal $AgNO_3$ instead of KNO_3, it is found that the freezing point (−0.33°) of the $AgNO_3$ solution is not affected by the first two additions of NH_3 but that the third addition depresses it to −0.51°. The electrical conducting powers of the $AgNO_3$ and KNO_3 solutions are substantially unchanged by the additions of the NH_3. What conclusions can you draw from these experiments as to the nature of the complex formed?

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CHAPTER XVI

THE CONDUCTION OF ELECTRICITY

1. Classes of Electrical Conductors.—Solid and liquid conductors of electricity may be divided into two classes: (1) Purely **metallic conductors** in which the passage of the current is not accompanied by a transfer of matter and produces no effect other than an increase in the temperature of the conductor; and (2) purely **electrolytic conductors** in which the passage of the current is accompanied by a simultaneous transfer of matter in *both directions* through the conductor. Aqueous solutions of electrolytes and fused salts are good examples of electrolytic conductors.

Some interesting conductors which occupy an intermediate position between purely metallic and purely electrolytic conductors are also known.[3] In these cases part of the electricity which flows through the conductor carries no matter with it while the remainder does. The part of the electricity which passes through this intermediate class of conductors in the first way, that is, without being accompanied by a transfer of matter, may, by gradually altering the composition of the conductor, be varied gradually and continuously from 100 per cent. (purely metallic conduction) to zero per cent. (purely electrolytic conduction). Our two classes of conductors would seem, therefore, to constitute simply two limiting cases. As a matter of fact, however, most conductors seem to belong exclusively to one or the other of these limiting cases, those of the intermediate or mixed character, of which solutions of sodium in liquid ammonia constitute an example, being comparatively rare.

If a direct current is caused to pass through an electrolytic conductor between two pieces of metal, called the **electrodes,** the electrode at which the current enters the electrolytic conductor is called the **anode** and the other electrode is called the **cathode.** The passage of a current in this way through a purely electrolytic conductor is called **electrolysis** and is always accompanied by chemical changes of some kind at both electrodes.

2. The Mechanism of Metallic Conductance.—In our first chapter (I, 2*g*) mention was made of the fact that in metallic substances some of the electrons are able to move about from atom to atom within the body of the metal with comparative ease. When a difference of potential is applied to the ends of a piece of metal a stream of these electrons through the metal is immediately set up. This stream of electrons constitutes the electric current in the metal and the collision of these electrons with the atoms of the metal produces the temperature increase which always accompanies the passage of an electric current through a metal.

A metal carrying a current is surrounded by a magnetic field, and the direction and nature of this field would be the same whether the current in the metal was caused by the motion of positive electricity in one direction or by the motion of negative electricity in the opposite direction and before the nature of metallic conduction was understood, the **"direction of the current"** in a metal was arbitrarily defined as the direction in which positive electricity would have to flow in order to produce the observed magnetic effects. We now know, however, that the current is actually due to the motion of negative electricity, the electrons, so that we find ourselves in the rather peculiar position of defining the "direction of the current" in a metal as the direction *opposite* to that in which the electricity actually flows.

3. The Mechanism of Electrolytic Conductance.—When a difference of potential sufficient to cause a steady current, is applied to two electrodes dipping into a solution containing dissolved electrolytes, *all* of the anions in the solution immediately start to move toward the anode or positive electrode while *all* of the cations start moving toward the cathode or negative electrode. The motion of these ions constitutes the current of electricity through the solution and the *direction of the current* in the solution is arbitrarily defined as the direction in which the cations move. The quantity of electricity which is transported through the solution in this way is divided among the different species of ions in the solution in proportion to their numbers, the charges which they carry, and the velocities with which they move. The product of the number of charges on a given species of ion into the number of these ions and into the velocity with which they move through the solution under a unit potential gradient is evidently a measure of the **current carrying capacity** of this species of ion in the solution.

4. The Mechanism of the Passage of Electricity between a Metallic and an Electrolytic Conductor. (*a*) **Electrochemical Reactions.**—Through any cross section of a solution containing electrolytes the current is carried by the ions of these electrolytes and *every species of ion in the solution,* no matter how great a number of different species there may be, helps in carrying the current, each species in proportion to its current-carrying capacity (XVI, 3). In conducting the current *from* the solution *to* the electrode or *vice versa,* however, only a few, in many cases only *one* ion species is involved, namely, that species which most easily takes on or gives up an electron under the conditions. Since the current through the metallic portion of the circuit consists only of moving electrons it is clear that an exchange of electrons between electrode and solution must take place in some manner at the electrode surface. This exchange of electrons constitutes an **electrochemical reaction,** of which there are very many varieties. We shall consider a few such reactions.

Case 1.—Let Fig. 28 represent an electrolytic cell composed of two silver electrodes dipping into a solution of silver nitrate. The cathode receives a negative charge from the dynamo, that is, a stream of electrons flows through the wire from the dynamo terminal to the cathode, and the negative potential of the cathode relative to the solution, therefore, rises. If this current is to continue flowing, these excess electrons on the cathode must be removed in some way by entering into an electrochemical reaction with some species of ion. The reaction in this instance consists in a union of the electrons from the wire with the silver ions in the solution, which are thereby reduced to ordinary silver atoms and deposited or plated out upon the electrode. The reaction may be written thus,

$$Ag^{+} + (-) = Ag \tag{1}$$

At the anode the silver atoms on the surface of the silver electrode give up their electrons and enter the solution as silver ions, while the electrons thus set free flow around through the wire to the positive terminal of the dynamo. This reaction, which may be written

$$Ag - (-) = Ag^{+} \tag{2}$$

is evidently the reverse of the one at the cathode and hence the electrolysis in this cell consists in the dissolving of metallic silver from the anode and the plating out of metallic silver upon the cathode.

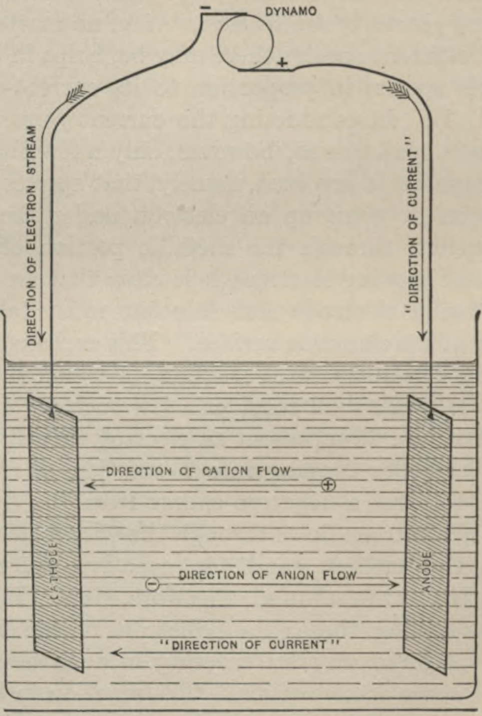

FIG. 28.

Case 2.—Let the cell in Fig. 28 consist of a silver anode and a silver chloride cathode, dipping into a solution of potassium chloride. A silver chloride cathode consists simply of a silver wire covered with a coating of solid AgCl. The electrode processes are as follows: The electrons which flow to the cathode from the dynamo terminal are removed by the following electrochemical reaction:

$$AgCl+(-)=Ag+Cl^- \qquad (3)$$

that is, the silver chloride is reduced to metallic silver, the chlorine atoms taking up the electrons from the wire and passing into solution as chloride ions. At the anode the reverse reaction occurs,

$$Cl^-+Ag=AgCl+(-) \qquad (4)$$

The chloride ions give up their electrons to the wire and unite with the silver electrode forming a coating of silver chloride over it.

Case 3.—Let the cell in Fig. 28 consist of a platinum anode and a platinum cathode dipping into a solution containing a mixture of ferric sulphate ($Fe_2(SO_1)_3 \rightleftarrows 2Fe^{+++} + 3SO_4^{--}$) and ferrous sulphate ($FeSO_4 \rightleftarrows Fe^{++}+SO_4^{--}$). The electrons coming to the cathode from the dynamo are removed from the cathode by the following electrochemical reaction:

$$Fe^{+++}+(-)=Fe^{++} \qquad (5)$$

that is, the electrons are taken up by the ferric ions which thereby lose one of their positive charges and become ferrous ions. At the anode the reverse reaction occurs.

(*b*) **Characteristic Electrode Potentials.**—Let the cell in Fig. 28 consist of a platinum anode and a platinum cathode dipping into a solution containing the following electrolytes: KCl, Na_2SO_4, and $LiNO_3$. The ions arising from the ionization of these salts will be the cations, K^+, Na^+ and Li^+ and the anions, Cl^-, SO_4^{--} and NO_3^-. In addition there are also present in every aqueous solution very small quantities of hydrogen ion H^+ and of hydroxyl ion OH^- arising from the ionization of the water itself which takes place to a *very slight extent,* according to the reaction

$$H_2O \rightleftarrows H^++OH^- \qquad (6)$$

Now as the electrons coming from the negative terminal of the dynamo begin to collect upon the cathode the potential between this electrode and the solution thereby increases and the negative electrons on the electrode are attracted by the positively charged ions in the solution in contact with electrode. If this potential difference is great enough and is continuously maintained by electrons coming from the dynamo, we have seen that a union between the electrons in the wire and one or more species of the ions in the solution will take place. In other words an electrochemical reaction will occur. Now in the present instance there are obviously at least four electrochemical reactions, any one of which might conceivably take place at our cathode, to wit:

$$\mathrm{Li^+ + (-) = Li\ (metal)} \qquad (7)$$

$$\mathrm{K^+ + (-) = K\ (metal)} \qquad (8)$$

$$\mathrm{Na^+ + (-) = Na\ (metal)} \qquad (9)$$

or

$$\mathrm{2H^+ + 2(-) = H_2\ (gas)} \qquad (10)$$

Which of these reactions will actually occur?

In order to bring about a given electrochemical reaction at any electrode we must first create a sufficient potential difference in the desired direction, that is, we must make the potential difference large enough to force the electrons to go in the direction desired. Now the potential difference necessary to accomplish this is a characteristic property of each electrochemical reaction and of the concentrations of the ions and molecules involved in that reaction as well as of the thermodynamic environment by which these ions and molecules are surrounded. This potential difference we shall call the **characteristic electrode potential** of the reaction. More explicitly, *the characteristic electrode potential of a given electrochemical reaction under a given set of conditions is the potential difference which exists between the electrode and the solution when the two are in equilibrium with each other with respect to the reaction in question.* Whenever, therefore, the potential difference at any electrode is kept either greater or less than the characteristic potential of some electrochemical reaction which is possible at that electrode, then this reaction will proceed continuously in the one direction or the other as long as the necessary potential difference is maintained.

Now in the present instance, as the potential difference between our cathode and the solution rises, due to the flow of electrons from the dynamo to the cathode, it will eventually reach a value which will exceed the characteristic electrode potential of some one of the four possible reactions represented by equations (7) to (10). When this happens the reaction in question will take place at our cathode. Of these reactions, the fourth one happens to have the smallest characteristic electrode potential under the given conditions, and hence the electrolysis of our solution results in the evolution of hydrogen gas at the cathode due to a decomposition of the water as represented by reactions (6) and (10). These may be added together and written thus,

$$2H_2O+2(-)=H_2+2OH^- \tag{11}$$

showing that hydroxyl ion is produced in the solution as one result of the reaction. In other words, the solution in the neighborhood of the cathode becomes alkaline. If a very heavy current is passed through the solution, it may happen eventually that the electrons are sent to the cathode from the dynamo faster than they can be removed by reaction number (10). In that case the potential at the electrode will rise and it may become great enough to cause reaction (9) to take place to some extent simultaneously with reaction (10), since its characteristic potential stands next above that of reaction (10). If, however, any metallic sodium should separate on the electrode as a result of the occurrence of reaction (9), it would immediately proceed to react with the water, thus

$$2Na+2H_2O=2Na^++2OH^-+H_2 \tag{12}$$

so that the final products would be the same as though reaction (10) were the only one which occurred. If the current density (*i.e.*, amount of current per unit electrode surface) at the electrode is kept small, however, only reaction (10) will take place at this electrode.

Let us now turn to the anode of our cell and see what will happen there. The reaction must of course be one which will furnish electrons to the anode. Any one of the following would do this:

$$2Cl^-=Cl_2(\text{gas})+2(-) \tag{13}$$

$$Cl^-+3H_2O=ClO_3^-+6H^++6(-) \tag{14}$$

$$2SO_4^{--}=S_2O_8^{--}+2(-) \tag{15}$$

and

$$4OH^-=O_2(\text{gas})+2H_2O+4(-) \tag{16}$$

Of all these possible reactions, however, the last one has the smallest characteristic electrode potential in our solution and is, therefore, the one which will take place at our anode. By adding together equations (6) and (16) we obtain the equation

$$2H_2O = 4H^+ + O_2 + 4(-) \tag{17}$$

which represents the final result of the electrolysis at the anode. Gaseous oxygen is evolved and the solution around the anode becomes acid.

The electrode products of the electrolysis with this cell come, therefore, entirely from the water itself and not at all from the dissolved salts. The current also is carried *from* electrode *to* solution and *vice versa entirely* by the ions of the water and not to any appreciable extent by the ions of the dissolved electrolytes. The current *through* the solution, however, is practically *all* carried by the ions of the dissolved electrolytes because there are so few H^+-ions and OH^--ions that their current carrying capacity (XVI, 3) is entirely negligible. The reason these two species of ions can nevertheless carry all of the current between the electrode and the solution is because at the electrodes, as fast as these ions are used up by the electrode reaction, a new supply is continuously produced by the ionization of some more water according to reaction (6), since any chemical or electrochemical reaction can be made to proceed continuously in one direction provided one of the products of the reaction is continually removed or destroyed as fast as it is formed, and this is what happens at our electrodes, H^+-ions being removed at the cathode and OH^--ions at the anode.

It not infrequently happens that two or more possible electrochemical reactions will, in a given solution, have practically the same characteristic electrode potentials. When this happens the reactions will take place simultaneously during the electrolysis and a mixture of products will be obtained. This happens, for example, during the electrolysis of a moderately strong solution of HCl with platinum electrodes. At the anode the two reactions

$$2Cl^- = Cl_2(\text{gas}) + 2(-) \tag{18}$$

and $$4OH^- = O_2(\text{gas}) + 2H_2O + 4(-) \tag{18a}$$

occur simultaneously, a mixture of oxygen and chlorine gases being evolved at the electrodes. Even when their characteristic electrode potentials are quite different, mixed electrochemical reactions can be made to occur by forcing more current through the cell than one reaction can take care of, as in the example given above (p. 197). The actual products of the electrolysis of any given solution depend, therefore, greatly upon the conditions under which the electrolysis is carried out and a clean-cut single electrochemical reaction entirely free from even traces of other reactions is, as a matter of fact, rather difficult to bring about in any prolonged electrolysis. In Table XIX*a* are shown some of the electrochemical reactions which occur during electrolyses of aqueous solutions with platinum electrodes.

TABLE XIX*a*

Principal Electrode Reactions and Products of the Electrolysis of Aqueous Solutions with Platinum Electrodes. (M = alkali metal)

Anode reaction	Solute	Cathode reaction
$2H_2O = 4H^+ + O_2 + 4(-)$	$AgNO_3$	$Ag^+ + (-) = Ag$
	$CuSO_4$	$Cu^{++} + 2(-) = Cu$
	MNO_3	$2H_2O + 2(-) = 2OH^- + H_2$
	M_2SO_4	
	H_2SO_4	$2H^+ + 2(-) = H_2$
	H_3PO_4	
	Dilute HCl	
	Dilute HNO_3	
$2Cl^- = Cl_2 + 2(-)$	Conc. HCl	
$4OH^- = 2H_2O + O_2 + 4(-)$	MOH	$2H_2O + 2(-) = 2OH^- + H_2$
$2H_2O = 4H^+ + O_2 + 4(-)$	Conc. HNO_3	$NO_3^- + 4H^+ + 3(-) = 2H_2O + NO$ and $NO_3^- + 9H^+ + 8(-) = 3H_2O + NH_3$
$2I^- = I_2 + 2(-)$	$MI + I_2$	$I_2 + 2(-) = 2I^-$

Problem 1.—What conditions must prevail in a solution in order that an object which is made the cathode in the solution shall be plated with brass by electrolysis?

(*c*) **Voltaic Action.**—In the Daniell cell a copper sulphate solution containing a copper electrode is placed in contact (by means of a porous wall or partition) with a zinc sulphate solution containing a zinc electrode. At each electrode there exists a potential difference between solution and electrode which potential difference is the characteristic electrode potential at the electrode in question under the given conditions, the two electrochemical reactions involved being respectively

$$\mathrm{Cu}-2(-)=\mathrm{Cu}^{++}$$

and

$$\mathrm{Zn}-2(-)=\mathrm{Zn}^{++}$$

The total potential across the terminals of this cell (*i.e.*, the potential difference between the two electrodes) will, therefore, be equal to the algebraic sum of the two characteristic electrode potentials plus any potential difference which may exist at the junction between the two solutions. Now in this particular cell it happens that the two characteristic electrode potentials are such that the total potential across the cell is about 1.1 volts, the zinc electrode being negative with respect to the copper. If the two electrodes are connected externally by a wire, a current of electricity will, therefore, flow through the wire from the copper to the zinc, and zinc will dissolve at the anode and copper deposit on the cathode. The total reaction of the cell will be the algebraic difference of the two electrode reactions, which is

$$\mathrm{Zn}+\mathrm{Cu}^{++}=\mathrm{Zn}^{++}+\mathrm{Cu} \qquad (19)$$

When two electrodes are arranged in a cell so that the two characteristic electrode potentials are such that the cell is capable, as above, of producing an electric current in an external circuit, the current is said to be produced by **voltaic action** and the cell is a primary battery. Voltaic action and electrolysis by means of a current produced externally and forced through the cell are essentially identical phenomena, however, and obey the same laws. A reaction such as that represented by equation (19) will also evidently occur *without the production of an external current* if a piece of zinc be simply dipped into a solution of a cupric salt (Cf. X, 9).

(*d*) **Normal Potentials and Normal Electrodes.**—For a given cell, each of the two characteristic electrode potentials (which together with the potential at the liquid junction make up the total E.M.F. of the cell) depends upon the concentrations of the molecular and ion species which take part in the electrochemical reaction at the electrode, as well as upon the thermodynamic environment in the solution around the electrode. In writing the equation of an electrochemical reaction a line above a formula will hereafter be employed to indicate that the molecular species is present in the gaseous state, a line below the formula will be similarly used to indicate the crystalline state, while the absence of such lines will indicate that the molecular or ion species in question is present only in solution. The so-called **"normal potential"** of a given electrochemical reaction is the characteristic electrode potential for that reaction when all gaseous substances involved in the reaction *as written* are present under a pressure of one atmosphere and all similarly involved molecular and ion species which are present only as solutes have each a concentration of one formula weight per liter. Thus the potential of the "normal hydrogen electrode" is the potential at a platinum electrode saturated with hydrogen gas under a pressure of one atmosphere dipping into a solution containing hydrogen ion at a concentration of one formula weight per liter when equilibrium is attained with respect to the reaction, $\overline{H_2}-2(-)=2H^+$; the potential of the "normal zinc electrode" is the potential at a zinc electrode dipping into a solution containing zinc ion at a concentration of one formula weight per liter when equilibrium is attained with respect to the reaction $\underline{Zn}-2(-)=Zn^{++}$; the potential of a "normal calomel electrode" is the potential of a mercury electrode covered with a layer of crystalline HgCl in contact with a solution containing chloride ion at a concentration of one formula weight per liter when equilibrium is attained with respect to the reaction, $\underline{Hg}+Cl^- -(-)=\underline{HgCl}$; and the potential of a "normal arsenious-arsenic electrode" is the potential at any suitable electrode which is in electrochemical equilibrium with respect to the reaction, $H_3AsO_3+H_2O-2(-)=H_3AsO_4+2H^+$, when each of the solute species is present at a concentration of one formula weight per liter; etc.

By joining together the solutions surrounding any two normal electrodes by means of some suitable intermediate liquid (such as a solution of KNO_3) a voltaic cell is formed (Cf. above, 4*c*) and the total electromotive force of such a cell will (except for the small potentials at the liquid junctions between the two electrode vessels) be equal to the algebraic sum of the normal potentials of the two electrodes. If one of the electrodes of such a cell is the normal hydrogen electrode, then the total electromotive force of the cell (after subtracting the liquid junction potentials) is arbitrarily taken as the normal potential of the other electrode, that is, in computing the values of the different normal electrode potentials the potential of the normal hydrogen electrode is arbitrarily taken as zero.

In Table XIX*b* are given the "hypothetical normal potentials" of a number of electrochemical reactions based upon the normal hydrogen electrode as zero. They are termed "hypothetical normal" because they have been computed from measurements at various concentrations on the assumptions: (1) that the equivalent conductance ratio (see XVII, 2*b*, equation 10) is a correct measure of the degree of ionization of all electrolytes even for concentrations greater than normal; and (2) that the thermodynamic environment in all solutions even for concentrations greater than one mole per liter is the same as it is in pure water; in other words the laws of dilute solutions (XIII, 3) are assumed to hold for all such solutions. Neither of these two assumptions can be regarded as correct, hence the expression "hypothetical normal" as applied to such values as those given in Table XIX*b*. We are not at present in a position to calculate the true normal potentials of electrochemical reactions and in view of this fact, it would be better to adopt some other basis (milli-normal potentials, for example) for computing and recording characteristic electrode potentials, but this has not as yet been done. A more complete table of "hypothetical normal" potentials can be found in a monograph[4] by Abegg, Auerbach and Luther.

TABLE XIX*b*

So-called "Normal Potentials" for some typical electrochemical reactions, based upon the "normal" hydrogen electrode as unity. The reaction tends to go in the direction indicated and charges the electrode with a charge of the sign and magnitude given.

Electrochemical reaction	− volts	Electrochemical reaction	+ volts
$\underline{Li}-(-)=Li^+$	3.03	$2H^++2(-)=\overline{H_2}$	±0.0
$\underline{K}-(-)=K^+$	2.93	$\underline{HgCl}+(-)=Hg(liq)+Cl^-$	0.272
$\underline{Na}-(-)=Na^+$	2.72	$Cu^{++}+2(-)=\underline{Cu}$	0.34
$\underline{Mg}-2(-)=Mg^{++}$	1.55	$Ag(NH_3)_2^++(-)=\underline{Ag}+2NH_3$	0.38
$\underline{Zn}-2(-)=Zn^{++}$	0.76	$\overline{O_2}+2H_2O+4(-)=4OH^-$	0.40
$\underline{Fe}-2(-)=Fe^{++}$	0.43	$\underline{I_2}+2(-)=2I^-$	0.62
$\underline{Cd}-2(-)=Cd^{++}$	0.40	$Fe^{+++}+(-)=Fe^{++}$	0.74
$\underline{Co}-2(-)=Co^{++}$	0.3	$Ag^++(-)=\underline{Ag}$	0.80
$\underline{Ni}-2(-)=Ni^{++}$	0.2	$Hg^++(-)=Hg(liq)$	0.80
$\underline{Pb}-2(-)=Pb^{++}$	0.12	$Br_2+2(-)=2Br^-$	1.10
$\underline{Sn}-2(-)=Sn^{++}$	0.10	$\overline{Cl_2}+2(-)=2Cl^-$	1.35
$\underline{Fe}-3(-)=Fe^{+++}$	0.04	$Au^++(-)=\underline{Au}$	1.5
$\overline{H_2}-2(-)=2H^+$	∓0.0	$MnO_4^-+8H^++5(-)=Mn^{++}+4H_2O$	1.52

Problem 2.—How could you arrange the cell so as to obtain an electric current from the occurrence of each of the following reactions in the direction indicated:

$$Fe+Cu^{++}=Fe^{++}+Cu$$
$$Zn+2H^+=Zn^{++}+H_2$$
$$3Zn+8H^++2NO_3^-=3Zn^{++}+2NO+4H_2O$$
$$3Zn+Cr_2O_7^{--}+7H^+=3Zn^{++}+2Cr^{+++}+7H_2O$$

From the data in Table XIX*b* calculate approximately the potential of the cell in the first three cases. Predict also from the data in this table what will occur: (a) when a piece of copper is dipped into a normal $AgNO_3$ solution; (b) when a piece of tin is dipped into a normal $FeCl_3$ solution; (c) when a piece of tin is dipped into a normal HCl solution; (d) when a piece of copper is dipped into a normal HCl solution; (e) when a piece of silver is dipped into a normal $Pb(NO_3)_2$ solution; (f) when a $2n$ solution of $FeCl_2$ is mixed with a solution of $HMnO_4$; (g) when solid iodine is shaken with a normal solution of KBr; (h) when pure gaseous chlorine is passed through a normal solution of KI.

Every chemical reaction occurring in a solution can always be regarded as made up of two opposing electrochemical reactions and it can be shown to follow from the laws of thermodynamics that whenever equilibrium (I, 9 and XXII, 1) has been attained in such a reaction, the concentrations of all of the solute species involved must be such that the characteristic electrode potentials of the two opposing electrochemical reactions are equal to each other.

The brief treatment of the subject of characteristic electrode potentials in this section and the problems illustrating the significance and use of electromotive force data are given at this point in order that the student may appreciate the general nature of the processes involved in the passage of electricity across a boundary between a metallic and an electrolytic conductor. In practice it frequently happens that owing to the slowness of some electrochemical reactions the actual reactions which occur in electrochemical processes are not always those which one would predict from such data as those given in Table XIX*b*. The phenomena of "passivity" and "over-voltage" and many other factors and relationships which must be understood in order to handle intelligently electrochemical problems are treated at length in books devoted to the special field of electrochemistry,[1,2] a field which will not be included within the scope of this book.

5. Faraday's Law of Electrolysis.—From the preceding discussion of the mechanism of electrolysis it is clear that the chemical changes which take place at the electrodes are the result of the taking on or giving up of electrons by atoms, atom groups and ions and that for every ion involved in this electrode process, one, two, or three, etc., electrons are also involved according as the ion carries one, two or three, etc., charges which must be neutralized, that is, according as the change in valence is one, two or three, etc., units. Hence for every electrochemical change involving *one* equivalent weight of a substance the same quantity of electricity will always be required and this quantity will be

$$q = \mathbf{N}e \tag{20}$$

or for N_e equivalents of chemical change the quantity of electricity required will be

$$q = \mathbf{N}eN_e \tag{21}$$

where **N** is Avogadro's number and e, the charge carried by one electron, is called the *elementary charge of electricity.*

If we put

$$\mathbf{N}e = F \tag{22}$$

equation (21) becomes

$$q = FN_e \tag{23}$$

where F is a universal constant. The significance of this equation may be stated in words as follows: *Whenever an electric current passes across a junction between a purely metallic and a purely electrolytic conductor a chemical change or chemical changes occur the amount of which, expressed in chemical equivalents, is exactly proportional to the quantity of electricity which passes and is independent of everything else.* This statement is known as **Faraday's Law of Electrolysis** and was discovered by Michael Faraday[a] in 1833. The proportionality constant, F, in equation (23) is known as **one faraday or one equivalent** of electricity and is evidently the amount of electricity required to produce one equivalent of chemical change. The quantities, e and F (equation 22), evidently bear the same relation to each other that the weight of an atom does to the atomic weight of the element (I, 7).

[a] Michael Faraday (1791–1867). The son of a blacksmith in Surrey, England. Served as laboratory assistant to Sir Humphrey Davy and later became Professor of Chemistry at the Royal Institution, London. He discovered benzene in 1825 and made a large number of important discoveries in electricity and magnetism. The experiments upon which he based his law of electrolysis are an interesting illustration of the keen insight which led Faraday to enunciate a general law upon what seems today to be very meagre and inaccurate data. (Faraday's *Experimental Researches in Electricity.* Everyman's Library Series, pp. 48 to 84.)

The value of the faraday has been very accurately determined[5] by measuring (with a silver coulometer) the quantity of electricity required to deposit one equivalent weight of metallic silver from a silver nitrate solution and also by measuring (with an iodine coulometer) the amount required to liberate one equivalent weight of iodine from a solution of potassium iodide. The result obtained was F = **96,500** (± 0.01 per cent.) coulombs per equivalent.

An apparatus arranged for the measurement of the amount of a given chemical change produced by an electric current is termed a **coulometer** (or sometimes a voltameter) and is employed for measuring the quantity of electricity passed through a circuit. The two most accurate types are the silver coulometer and the iodine coulometer. In the former metallic silver is deposited electrolytically from a solution of silver nitrate and the weight of the deposit determined. In the latter[6] iodine is liberated electrolytically from a solution of potassium iodide, the amount liberated being determined by titration.

6. The Elementary Charge of Electricity.—If either e or $\mathbf{N}$ can be directly measured it is clear that the other one can then be calculated by means of equation (22), since F is known.

When X-rays pass through air or any other gas, the gas becomes ionized (I, 2*g*), that is, some of its molecules lose temporarily one or more of their electrons and thus acquire a positive charge. These charged molecules are called gaseous ions. These ions as well as the electrons liberated from them all possess the unordered heat motion (II, 1) of the other molecules of the gas, that is, they dart rapidly about in all directions colliding with anything which may come in their path. If a tiny droplet of oil or mercury or some other liquid is introduced into an ionized gas, it will eventually collide with one of these rapidly moving ions and will capture and hold it. The droplet thus acquires a charge of electricity exactly equal to that possessed by the captured ion and from the observed behavior of the charged droplet in an electric field, the magnitude of its charge can be measured. In this way Millikan has succeeded[7] in obtaining a very accurate measurement of the value of the elementary charge of electricity. His apparatus is shown in Fig. 29.

By means of an atomizer A a fine spray of oil or other liquid is blown into the chamber D and one of the droplets eventually falls through the pin hole *p* into the space between the two condenser plates, M and N. The pin hole is then closed and the air between the plates is ionized by a beam of X-rays from X. The droplet is illuminated through the windows *g* and *c* by a powerful beam of light from an arc at *a*, and is observed through a telescope directed at a third window not shown in the figure.

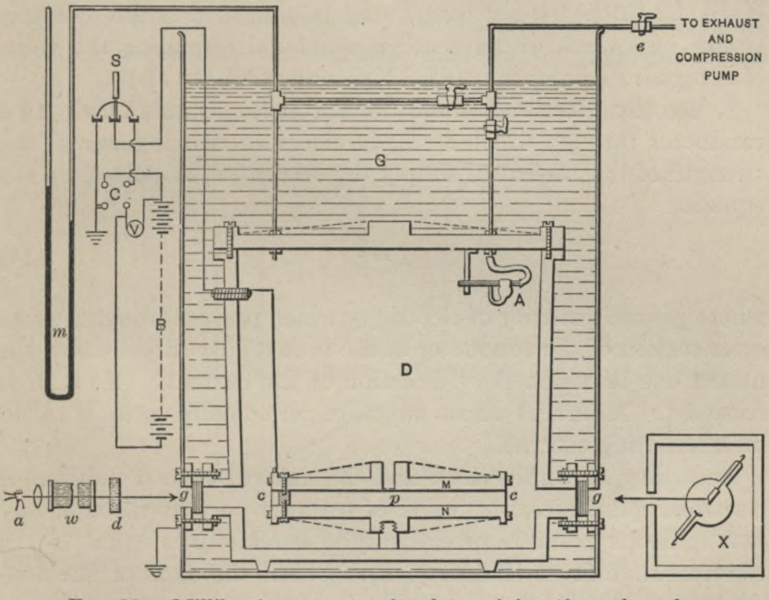

Fig. 29.—Millikan's apparatus for determining the value of *e*.

The droplet eventually acquires a charge by collision with one of the ions of the gas and can then be caused to move upward or downward at will by charging the plates M and N with electric charges of the desired signs, by means of the switch S. The speed of the drop under the influence of the electric field is directly proportional to the magnitude of its charge, and the observer watching the drop observes sudden changes in its speed due to a change in the charge of the drop brought about by the capture, now and then, of an additional ion with which it happens to collide. By measuring this change in the speed of the drop immediately after the capture of an ion and combining it with the speed of the drop when falling under the influence of gravity, the magnitude of the charge of the captured ion can be calculated. From a very large number of experiments of this kind Professor Millikan found that the charge carried by a gaseous ion is always equal to or is a small *exact multiple* of 1.59×10^{-19} (± 0.2 per cent.) coulombs and this is, therefore, the elementary charge of electricity, the charge of *one electron*. Substituting this value for e in equation (22) above we find for $\mathbf{N}$ the value $\mathbf{N} = 6.062 \cdot 10^{23}$ (± 0.2 per cent.), and this method is the most accurate one which we have at present for determining the value of Avogadro's number. (Cf. IX, 4 and XXVII, 11.)

7. Electrical Resistance and Conductance. Ohm's Law.—In a conductor through which a steady direct current is passing, the strength of the current or simply the **current**, I, is defined by the equation

$$I = \frac{q}{t} \tag{24}$$

where q is the quantity of electricity which passes through a given cross section of the conductor in the time t. By direct current is meant one in which the "direction of the current" (XVI, 2) is constant. A current whose direction periodically varies is called an alternating current.

According to Ohm's[a] Law and the nature of our definitions of electrical quantities, the value of a direct current through any homogeneous metallic or electrolytic conductor is equal to the electromotive force (E.M.F.), E, between the ends of the conductor, divided by the resistance, R, of the conductor, or

$$I = \frac{E}{R} \text{ (Ohm's Law)} \tag{25}$$

The reciprocal of the resistance is called the **conductance,** L.

$$L = \frac{1}{R} \tag{26}$$

The unit of conductance is called the **reciprocal ohm** or the **mho.**

The conductance, L, of any homogeneous conductor of uni-

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[a] Georg Simon Ohm (1787–1854). Professor of Mathematics in the Jesuits' College, Cologne, and in the polytechnic school at Nuremberg. The law which bears his name was formulated in a pamphlet published by him in Berlin in 1827.

form cross section is proportional to the area, A, of the cross section and inversely proportional to the length, l, of the conductor, or

$$L=\frac{\overline{L}A}{l} \tag{27}$$

The proportionality constant, $\overline{L}$, is evidently the conductance of a conductor 1 cm. long and 1 sq. cm. in cross section. It is called the **specific conductance** of the material of which the conductor is composed. It depends upon the chemical nature of the material, its temperature, pressure and physical condition. The reciprocal of the specific conductance is called the specific resistance, $\overline{R}$.

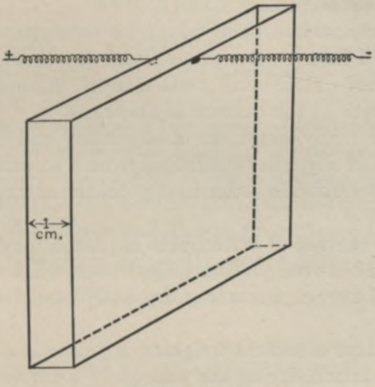

FIG. 30.

$$R=\frac{\overline{R}l}{A} \tag{28}$$

In dealing with the conductance of solutions of electrolytes an additional quantity known as the equivalent conductance is also employed The **equivalent conductance,** Λ, of any solution of an electrolyte is defined as the conductance of that volume of the solution which contains one equivalent weight of the electrolyte, when measured between two parallel electrodes 1 cm. apart. (See Fig. 30.)

Problem 3.—Show that the specific conductance and the equivalent conductance of a solution containing C equivalents of electrolyte per liter are by the nature of their definitions, connected by the relation,

$$\Lambda = \frac{1000\overline{L}}{C} \tag{29}$$

If the concentration C is expressed in *moles* per liter, the quantity defined by equation (29) is called the molal or the molecular conductance, and is then usually represented by the symbol, λ, in case the molal and equivalent weights are different.

Problem 4.—A cylindrical resistance cell 2 cm. in diameter is fitted with horizontal silver electrodes 4 cm. apart, and is filled with 0.1 normal silver nitrate solution. An E.M.F. of 0.5 volt causes 3.72 milliamperes to flow through the solution. Calculate the conductance, the specific conductance, and the equivalent conductance.

Problem 5.—How much copper would be precipitated from a cuprous chloride solution in 1 hour by a current which produces 0.1 gram of hydrogen in the same time? How much from a cupric chloride solution? What is the average strength of the current in amperes?

Problem 6.—How many coulombs of electricity will be required in order to deposit 10 grams of silver in 60 minutes from a solution of silver nitrate? How many will be required in order to deposit the same amount of silver in 135 minutes?

Problem 7.—If a current of 0.2 ampere is passed for 50 minutes through dilute sulphuric acid between platinum electrodes, what volume of hydrogen and what volume of oxygen, measured dry at 27° and 1 atmosphere, will be produced?

Problem 8.—A silver electrode weighing x grams is made the anode in a hydrochloric acid solution during the passage of a current of 0.1 ampere for 10 hours. After drying, the electrode together with the closely adherent layer of silver chloride is found to weigh 10 grams. Calculate x.

Problem 9.—A cupric sulphate solution is electrolyzed with a copper cathode and platinum anode until 6.35 grams of copper are deposited. The gas evolved at the anode is measured at 25° over water whose vapor pressure at this temperature is 23.8 mm. Barometric pressure = 752 mm. (1) What volume does it occupy? (2) How much time would be required for the electrolysis if a current of 0.1 ampere were used? (3) What is the mass of the gas evolved?

Problem 10.—A current of electricity is passed for 53 hours through an aqueous solution of Na_2SO_4 between platinum electrodes. A silver coulometer connected in series shows a deposit of 10.8 grams of silver in this time. The gas evolved at the cathode in the Na_2SO_4 solution is collected and measured dry at 20° under a pressure of 756 mm. (1) What volume will it occupy? (2) What is its mass? (3) What was the average current strength employed in the electrolysis?

Problem 11.—A solution of cupric sulphate containing 5 grams of copper is allowed to stand in contact with an excess of bright iron tacks until all of the copper has been deposited. If the solution is now boiled with bromine water in excess and then with an excess of NH_4OH and the resulting precipitate filtered off, ignited, and weighed, how much will it weigh?

Problem 12.—Twenty grams of bright copper gauze are allowed to stand in contact with 1 liter of a 0.05 *normal* silver sulphate solution until action ceases. The gauze is then removed, dried and weighed. How much does it weigh? The solution remaining, which may be assumed to contain only cupric sulphate, is electrolyzed between platinum electrodes in such a manner that copper only is liberated at the cathode. How much copper is deposited? The gas given off at the anode is mixed with an excess of hydrogen (x grams) and exploded. The residual gas is measured over water at 20 and 772 mm. and found to occupy a volume of 2240 c.c. Calculate x. The vapor pressure of water at 20° is 17.5 mm.

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CHAPTER XVII

CONDUCTANCE AND DEGREE OF IONIZATION

1. Equivalent Conductance and Concentration. (*a*) Λ_0 **Values.**—Let one equivalent weight of an electrolyte dissolved in water be placed between two parallel electrodes 1 cm. apart and of indefinite area, as shown in Fig. 30. The conductance of this solution measured in this cell is by definition (XVI, 7) its equivalent conductance. If the solution in the cell be now gradually diluted, the conductance will be observed to change and will eventually increase gradually and continuously and approach a definite limiting value at infinite dilution. This behavior is illustrated by the data in Table XX.

Table XX

Illustrating the variation of equivalent conductance with concentration in aqueous solution at 18°

C, (equiv. per liter) =	1.0	0.5	0.1	0.03	0.01	0.001	0.0001	0.00
KCl. . . . . =	98.27	102.41	112.03	. . . .	122.43	127.34	129.07	129.5
$AgNO_3$. . . . . =	67.6	77.5	94.33	. . . .	107.80	113.14	115.01	115.7
NH_4OH. . . . . =	0.89	1.35	3.10	5.66	9.68	28	?	(238)
$HC_2H_3O_2$. . . . . . . =	1.32	2.01	4.68	8.52	14.59	41	107	(348)

In the case of the first two electrolytes (strong electrolytes, XV, 4) in this table the limiting value, Λ_0, of the equivalent conductance shown in the last column is obtained by extrapolation from the preceding values, and although extrapolation is always a more or less uncertain process, the values obtained for strong electrolytes are usually fairly reliable (to 1 per cent. or better in most cases) because the extrapolation extends over a short distance only, that is, the extrapolated value is not greatly different from the last measured value. In the case of the last two electrolytes (weak electrolytes, XV, 4), however, the Λ_0 values cannot be obtained in this manner owing to the very long extrapolation which would be necessary, for conductance measurements at concentrations below 0.0001 normal are exceedingly difficult to carry out with any accuracy. The Λ_0 values for weak electrolytes are, therefore, obtained by another method described below.

(*b*) **Ion Conductances.**—The increase of Λ with dilution is interpreted by the Ionic Theory as follows: With increasing dilution the degree of ionization (XV, 4) of the electrolyte increases, and since this results in a larger number of ions (current carriers) between the electrodes of the cell the conductance increases correspondingly. When the electrolyte is completely ionized (as at infinite dilution) its equivalent conductance in the solution, Λ_0, is evidently the equivalent conductance of a solution containing one equivalent weight of each of the ions. The magnitude of Λ_0 for an electrolyte will obviously depend upon the speeds with which the ions of that electrolyte move through the water, since the faster they move the more efficient they are as carriers of electricity, and for a given electrolyte Λ_0 will obviously be made up of the separate equivalent conductances of the ions of that electrolyte. Thus the Λ_0 values of the following electrolytes at 18° are expressed by the equations

$$\text{NaCl},\ \Lambda_0=\Lambda_{0_{\text{Na}^+}}+\Lambda_{0_{\text{Cl}^-}}=43.2+65.3=108.5$$
$$\text{LiOH},\ \Lambda_0=\Lambda_{0_{\text{Li}^+}}+\Lambda_{0_{\text{OH}^-}}=33.2+174=207$$
$$\text{HNO}_3,\ \Lambda_0=\Lambda_{\ \text{H}^+}+\Lambda_{0_{\text{NO}_3^-}}=313+61.7=375$$

the conductances being expressed in reciprocal ohms.

Table XXI shows the equivalent conductances at infinite dilution of some of the more important ions at 18° together with their temperature coefficients. The method by which the individual ion-conductances are obtained from the Λ_0 values of the electrolytes will be discussed in the next chapter. By adding together the proper ion-conductances one can obtain the Λ_0 value for any electrolyte. This statement is known as *Kohlrausch's*[a] *Law of the independent migration of ions.* This law is

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[a] Friedrich Wilhelm Georg Kohlrausch (1840–1910). Professor of Physics at Göttingen, at Würtzburg and in 1888 at Strassbourg. After 1895, President of the Physikalisch-Technische Reichsanstalt, at Charlottenburg.

TABLE XXI

Ion-conductances at infinite dilution and their temperature coefficients, at 18°. Based upon the measurements of Kohlrausch. (See Bates, Jour. Amer. Chem. Soc., **35**, 534 (1913).)

Cations			Anions		
Ion	$\Lambda_{0_{c+}}$	$\frac{1}{\Lambda}\left(\frac{d\Lambda}{dt}\right)_{18°}$	Ion	$\Lambda_{0_{a-}}$	$\frac{1}{\Lambda}\left(\frac{d\Lambda}{dt}\right)_{18°}$
H^+	313.	0.0154	OH^-	174.	0.018
Cs^+	67.4	0.0212	Cl^-	65.3	0.0216
K^+	64.3	0.0217	Br^-	67.2	0.0215
NH_4^+	64.5	0.0222	I^-	65.9	0.0213
Na^+	43.2	0.0244	NO_3^-	61.7	0.0205
Li^+	33.2	0.0265	ClO_3^-	54.8	0.0215
Tl^+	65.5	0.0215	BrO_3^-	48.	......
Ag^+	54.0	0.0229	IO_3^-	33.9	0.0234
$\frac{1}{2}Ca^{++}$	51.0	0.0247	$C_2H_3O_2^-$	35.	0.0238
$\frac{1}{2}Mg^{++}$	45.0	0.0256	$\frac{1}{2}C_2O_4^{--}$	61.	0.0231
$\frac{1}{2}Ba^{++}$	55.0	0.0239	$\frac{1}{2}SO_4^{--}$	67.7	0.0227
$\frac{1}{2}Pb^{++}$	61.0	0.0240	$\frac{1}{2}CrO_4^{--}$	72.	......

especially important in the case of weak electrolytes where the Λ_0 values cannot be obtained by extrapolation from the conductance data because even at high dilution (0.0001 normal) the ionization is still far from complete. (Cf. above and Table XX.)

Problem 1.—Compute the Λ_0 values for the following electrolytes at 18° from the individual ion-conductances: oxalic acid, ammonium bromide, barium iodate, ammonium hydroxide, acetic acid. The Λ_0 value for $\frac{1}{2}ZnSO_4$ at 18° is 113.0 reciprocal ohms. Calculate $\Lambda_{0_{\frac{1}{2}Zn^{++}}}$.

(*c*) **Empirical Dilution Laws.**—For expressing the rate of change of the equivalent conductance of an electrolyte with its concentration a number of empirical equations have been proposed and used by various investigators. Of these relations we shall mention here only two of the most recent ones. An equation proposed by Kraus[a] has been tested by Kraus and Bray[b] for a great variety of electrolytes in many different kinds of solvents and has been found to be on the whole very satisfactory. It has the following form:

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[a] Charles August Kraus. Since 1914, Professor of Chemistry at Clark University, Worcester, Mass.

[b] William Crowell Bray (1879–). Assistant Professor of Chemistry at the University of California.

$$\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2 \frac{C}{\left(1-\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)} = k + k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h \tag{1a}$$

where η/η_0 is the ratio of the viscosity (III, 6) of the solution to that of water at the same temperature and $\Lambda\, {}^{\eta}/\eta_0$ is called the "corrected" equivalent conductance. (Cf. Sec. 2c below.) The quantities k, k', h and likewise Λ_0 are empirical constants whose values are so chosen as to give the best agreement between the calculated and observed conductance values.

In the last column of Table XXII are shown the values of $\Lambda\, {}^{\eta}/\eta_0$ calculated from the Kraus equation for KCl solutions at 18°, using for the four empirical constants the values given at the head of the table. On comparing these values with the observed values for the same concentrations as shown in column 4, it will be seen that the agreement is very good except for concentrations below 0.001 molal. Here the equation seems to break down and apparently leads to a Λ_0 value much lower than the ordinarily accepted one for this salt.

Bates[a] has proposed an equation of the same form as that of Kraus except that the logarithm of the left-hand expression is employed instead of the expression itself.

$$\log_{10}\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2 \frac{C}{\left(1-\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)} = k + k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h \tag{1b}$$

The constants k, k' and h in the Bates equation are empirical ones to be evaluated from the experimental data, but the constant Λ_0 represents the value of Λ at infinite dilution, obtained by extrapolation from the most reliable measurements at high dilutions without reference to the values of the other constants in the general equation or to the form of this equation. In column 5 of Table XXII are shown the values of $\Lambda\, {}^{\eta}/\eta_0$ calculated from the Bates equation for KCl solutions at 18°, using for the three empirical constants k, k' and h the values given at the head of the table. The value for Λ_0 is that obtained from Table XXI. The agreement between these calculated values and the observed

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[a] Stuart Jeffrys Bates (1888–). Since 1914, Professor of Inorganic and Physical Chemistry at Throop College of Technology, Pasadena, Cal.

values is excellent throughout the whole concentration range between zero and 1 normal.

TABLE XXII

A comparison of the empirical equations of Bates and of Kraus with Kohlrausch's conductance data for KCl at 18°.

Bates' equation: $$\log_{10}\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2\frac{C}{\left(1-\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)}=k+k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h$$

where Λ_0, k, k', and h are empirical constants whose values for KCl at 18° are 129.50, −3.5905, 4.020, and 0.0775 respectively. (Bates, Jour. Amer. Chem. Soc., **37,** 1431 (1915).)

Kraus' equation: $$\left(\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)^2\frac{C}{\left(1-\frac{\Lambda\eta}{\Lambda_0\eta_0}\right)}=k+k'\left(\frac{C\Lambda\eta}{\Lambda_0\eta_0}\right)^h$$

where Λ_0, k, k', and h are empirical constants whose values for KCl at 18° are 128.3, 0.080, 2.707, and 0.763 respectively. (Kraus and Bray, Jour. Amer. Chem. Soc., **35,** 1412 (1913).)

Concentration, C moles per liter	Relative viscosity of the solution, η/η_0	Equivalent conductance observed		Equivalent conductance calculated (Bates), $\Lambda\ \eta/\eta_0$	Equivalent conductance calculated (Kraus and Bray), $\Lambda\ \eta/\eta_0$
		Λ	$\Lambda\ \eta/\eta_0$		
3.	0.9954	88.3	87.89	89.3	87.4
2.	0.9805	92.53	90.73	91.9	90.9
1.	0.982	98.22	96.5	96.53	96.4
0.5	0.9898	102.36	101.32	101.29	101.1
0.2	0.9959	107.90	107.46	107.43	107.6
0.1	0.9982	111.97	111.77	111.73	111.9
0.05	(0.9991)	115.69	115.59	115.58	115.5
0.02	(0.9996)	119.90	119.85	119.83	119.8
0.01	(0.9998)	122.37	122.35	122.32	122.4
0.005	(0.9999)	124.34	124.33	124.38	124.4
0.002	1.0000	126.24	126.24	126.31	126.3
0.001	....	127.27	127.27	127.32	127.2
0.0005	....	128.04	128.04	128.05	(127.6)
0.0002	....	128.70	128.70	128.68	(127.9)
0.0001	....	129.00	129.00	128.96	(128.1)
0.0	....	129.50	129.50	129.50	128.3

For moderate concentrations the viscosity ratio η/η_0 may be taken as unity and for weak electrolytes at small concentrations the product $\frac{C\Lambda}{\Lambda_0}$ is so small that the term containing it on the right-hand side of the equation is usually negligible in comparison with the term k, and hence for weak electrolytes *both* equations reduce to the form

$$\frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)} = \text{const.} \tag{1c}$$

which is known as Ostwald's[a] dilution law for weak electrolytes. It expresses the results for such electrolytes with great exactness (XXII, 6*d* and Table XXVII) and we shall see later that it can be deduced theoretically from the Second Law of Thermodynamics and the Solution Laws (XXII, 3*b*).

Problem 2.—Calculate the specific conductance of $0.0075n$ KCl solution at 18° using (1) the Kraus equation and (2) the Bates equation with the values of the constants given in Table XXII. Calculate, using Ostwald's dilution law, the specific conductance of $0.02n$ $HC_2H_3O_2$ solution at 18° using the data given in Table XX.

2. Degree of Ionization and Conductance Ratio. (*a*) **Ions and Ion-Constituents.**—Consider a solution of a salt CA, of concentration C equivalents per liter. The equivalent conductance of this solution may be regarded as made up of two parts: (1) the equivalent conductance of the ion-constituent, C, and (2) the equivalent conductance of the ion-constituent, A, that is,

$$\Lambda = \Lambda_c + \Lambda_a \tag{2}$$

The distinction between ion and **ion-constituent** should be clearly understood. The equivalent conductance (Λ_{c+}) of C-*ion* refers to the conductance of one equivalent weight of the constituent C when *all of it* is in the form of ions, while the equivalent conductance (Λ_c) of the *ion-constituent* C refers to that part of the conductance which is due to the constituent C, part of which may exist in the solution in the form of ions and the remainder in the condition of un-ionized molecules. It is evident from the definitions of these two quantities that they are related to each other by the equations

$$\Lambda_c = \alpha\Lambda_{c+} \tag{3}$$

and

$$\Lambda_a = \alpha\Lambda_{a-} \tag{4}$$

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[a] Wilhelm Ostwald (1853–). Emeritus Professor of Physical Chemistry of the University of Leipzig. Founder and Editor of the *Zeitschrift für physikalische Chemie* and the *Annalen der Naturphilosophie*.

where Λ_c and Λ_a are the equivalent conductances of the ion-constituents, C and A, in a solution of the salt CA, α is the degree of ionization (XV, 4) of the salt in this solution, and Λ_{c+} and Λ_{a-} are the two ion-conductances *in this same solution.* Λ_{c+} and Λ_{a-} will in general differ from Λ_{0c+} and Λ_{0a-}, the ion-conductances at infinite dilution, because the ions in the salt solution will not in general be able to move with the same velocity as in pure water, since the velocity with which ions move through any medium will depend upon the frictional resistance which they experience in that medium and this frictional resistance will in general be different in a salt solution from what it is in pure water.

(*b*) **The Calculation of Degree of Ionization.**—It may happen with a given solution that the resistance experienced by one of the ion species in moving through the solution is practically the same as that which it experiences in pure water. If, for example, this were the case for the cation, then it is evident that Λ_{c+} will be practically equal to Λ_{0c+} and equation (3) would become

$$\alpha=\frac{\Lambda_c}{\Lambda_{0c+}} \tag{5}$$

and it is evident that by means of this equation we could calculate the degree of ionization of the salt in this solution.

The equivalent conductance (Λ_c, Λ_a) of any ion-constituent in a solution is by definition equal to the total equivalent conductance of the electrolyte in that solution multiplied by the fractional part of the current-carrying done by the ion-constituent in question in that solution. This fraction is called the *transference number* (n_c, n_a) of the ion-constituent and the methods by which it is measured are described in the next chapter. We have, therefore,

$$\Lambda_c=n_c\Lambda \tag{6}$$

and hence equation (5) may be written

$$\alpha=\frac{n_c\Lambda}{\Lambda_{0c+}} \tag{7}$$

If the solution is so dilute that *both* ions experience practically the same resistance as they do in pure water we have (equation 5)

$$\alpha=\frac{\Lambda_c}{\Lambda_{0c+}}=\frac{\Lambda_a}{\Lambda_{0a-}} \tag{8}$$

and also by the principles of proportion

$$\alpha = \frac{\Lambda_c + \Lambda_a}{\Lambda_{0c^+} + \Lambda_{0a^-}} \tag{9}$$

or

$$\alpha = \frac{\Lambda}{\Lambda_0} \tag{10}$$

that is, under these circumstances the degree of ionization of a uni-univalent electrolyte at concentration C is equal to the ratio of its equivalent conductance at this concentration, to its equivalent conductance at infinite dilution. Equation (10) is the one most commonly employed for calculating degree of ionization from conductance data and is the one which we shall employ throughout this book except where otherwise indicated. It is evident from its derivation that *the equation is only valid for those solutions in which both ions are able to move with the same speed as they do at infinite dilution.*

(*c*) **The Viscosity Correction.**—In cases where the above condition is not fulfilled attempts have been made to correct for the effect of frictional resistance, on the assumption that Stokes' Law (IX, 3) is obeyed and hence that the equivalent conductance of an ion is inversely proportional to the viscosity (III, 6) of the medium through which it moves. This assumption leads to the equations

$$\alpha = \frac{\Lambda_c}{\Lambda_{0c^+}} \times \frac{\eta}{\eta_0} = \frac{\Lambda_a}{\Lambda_{0a^-}} \times \frac{\eta}{\eta_0} \tag{11}$$

and

$$\alpha = \frac{\Lambda}{\Lambda_0} \frac{\eta}{\eta_0} \tag{12}$$

corresponding to equations (8) and (10). The assumption is of doubtful validity, however. In fact a systematic investigation[1] of this subject has shown beyond question that Stokes' Law is not in general applicable to the movement of an ion. Instead, the following empirical equation seems to hold very closely for nearly all the cases studied:

$$\Lambda = \Lambda_0 \left(\frac{\eta_0}{\eta}\right)^h \tag{13}$$

where h is an empirical constant whose value (instead of being unity for all ions, as Stokes' Law would require) varies for the different ions between about 0.6 and 1.1 and for a given species of ion depends upon the nature of the molecules composing the medium through which the ion moves.

It has been proposed[2] to make use of the above relation in order to apply the viscosity correction, and this would in fact be the most logical procedure. Unfortunately it is of little value, however, because the constant h depends upon the nature of the solution and there is at present no satisfactory method of evaluating it for solutions of strong electrolytes. The whole question of the proper method of correcting for the influence of viscosity is thus in a very unsatisfactory condition. Where a correction for viscosity is necessary equations (11) and (12) may perhaps be employed as first approximations in many cases with a fair degree of accuracy, and this is about all we can safely say at present.

Some prominent investigators[7] in this field even incline to the opinion that the speeds of the ions actually increase with increasing concentration of the electrolyte, and that even in solutions so dilute that the viscosity of the solution is practically identical with that of pure water the ions move with decidedly greater velocities than they do at infinite dilution. If such is the case, the degrees of ionization calculated from the conductance ratio are all too high. The evidence at present (1915) available on this point, while not conclusive either way, nevertheless supports strongly the view that the conductance ratio is substantially a correct measure of the degree of ionization of uni-univalent electrolytes in dilute solution, and this is the view which is adopted in the following pages.

Problem 3.—If in a solution containing 0.05 mole each of KCl and LiCl each salt is 85 per cent. ionized, what would be the specific conductance of the solution (1) at 18° and (2) at 25°? Use Table XXI.

3. Degree of Ionization and Type of Electrolyte.—Salts belonging to the same ionic type (XV, 3*b*) have at the same equivalent concentrations approximately the same value of the conductance ratio, $\frac{\Lambda}{\Lambda_0}$. Table XXIII shows some average values of this ratio for the three simplest types.

For uni-univalent and probably also for bi-bivalent salts these values represent, according to equation (10), the degrees of ionization of the salts, because salts of these types ionize directly into the ions to which Λ_0 corresponds. Such is not the case, however, with the uni-bivalent, the uni-trivalent and the bi-trivalent types because they ionize in such a way as to give intermediate ions. Thus K_2SO_4 ionizes so as to give the ions K^+, SO_4^{--}, and KSO_4^-. At infinite dilution the intermediate ions KSO_4^- are all broken up into K^+ and SO_4^{--} ions so that the Λ_0 value corresponds only to these two ion species, but at any finite concentration the Λ value is made up of the separate conductances of *three* species of ions, the relative amounts of which are not known. Owing to the presence of these intermediate ions equation (10) cannot be employed to calculate α for such electrolytes. We have no very satisfactory method for determining the degree of ionization and the ion concentrations for salts like $BaCl_2$, although it can be done approximately in some instances by a combination of methods.[3]

TABLE XXIII

Values of $\frac{\Lambda}{\Lambda_0}$ at different concentrations for three types of electrolytes at 18°

Type	Example	0.001	0.01	0.05	0.1	Normal
Uni-univalent..........	KNO_3	0.96	0.92	0.87	0.84	
Uni-bivalent...........	$\left\{\begin{matrix} BaCl_2 \\ K_2SO_4 \end{matrix}\right\}$	0.94	0.87	0.78	0.73	
Bi-bivalent............	$MgSO_4$	0.86	0.64	0.47	0.41	

We can, however, make the general statement that *all salts are highly ionized in dilute aqueous solution.* There are a few exceptions to this rule, but they are very few and the rule is one which the student should remember. Some of the exceptions are lead acetate, ferric sulphocyanate; cadmium chloride ($\alpha =$ 45 per cent. at $0.1n$); and the mercuric halides ($\alpha = 0.1$ per cent. at $0.1n$).

Acids and bases, unlike salts, exhibit at any moderate concentration, such as 0.1 normal, every possible degree of ionization between a small fraction of 1 per cent. up to nearly 90 per cent. according to the nature of the substance. There is, to be sure, a fairly large group of uni-univalent acids and bases, including HCl, HBr, HI, HNO_3, $HClO_3$, KOH, NaOH, LiOH, which have ionization values comparable with those of the uni-univalent salts, with which, therefore, they may be classed; and likewise the uni-bivalent bases of the alkaline earths are also highly ionized in dilute solution, although perhaps somewhat less so than those of the alkali metals. But outside of these groups all possible values of α are met with, as illustrated by the following values of the percentage ionization (100α) at 25° and 0.1 normal: NH_4OH, 1.3 per cent.; H_2SO_3, 34 per cent. (into H^+ and HSO_3^-); H_3PO_4, 28 per cent. (into H^+ and $H_2PO_4^-$); HNO_2, 7 per cent.; $HC_2H_3O_2$, 1.3 per cent.; H_2CO_3, H_2S, HClO, HCN, HBO_2, all less than 0.2 per cent.

Polybasic acids are known to ionize in stages, giving rise to the intermediate ion; and the first hydrogen is almost always much more dissociated than the second, and the second much more than the third. Thus H_2SO_3 at 0.1 normal at 25° is about 34 per cent. dissociated into H^+ and HSO_3^-, and less than 0.01 per cent. dissociated into H^+ and SO_3^{--}.

4. Degree of Ionization and Temperature.—At room temperatures the value of α for uni-univalent strong electrolytes changes with the temperature at a rate of less than 0.1 per cent. per degree. For KCl at about 0.08 normal, A. A. Noyes[5] found for 100α the following values:

0°	18°	100°	156°	218°	281°	306°
89.3	87.3	82.6	79.7	77.3	72	64

which are typical of most salts of this type. In the case of weak electrolytes no general rule as to direction and magnitude can be given, although, as we shall see later (XXII, 10), the rate of change with the temperature can be calculated from the heat of ionization of the electrolyte.

5. Comparison of Degrees of Ionization Calculated by the Freezing-point and Conductance Methods.—As explained above (XV, 4), the freezing-point method can frequently be employed to calculate the approximate degree of ionization of uni-univalent electrolytes owing to a partial compensation of sources of error. A comparison of the values obtained by the two methods in the case of $CsNO_3$, KCl and LiCl is shown in Table XXIV. In the case of $CsNO_3$ the values obtained from the freezing-point method all appear to be too small. This may, at least partially, be ascribed to the powerful effect which the ions have upon the thermodynamic environment in the solution. In the case of LiCl the values obtained by the freezing-point method are apparently all too large. This is due chiefly to the fact that LiCl is highly hydrated in solution and no account was taken of this in the calculation. (Cf. XIV, 7.) In the case of KCl these two sources of error appear to compensate each other almost exactly and the values of α by the two methods agree within the experimental errors of the measurements. LiCl and $CsNO_3$ are extreme cases. Practically all other uni-univalent salts lie within the limits set by these two. It is evident from these results that agreement between the values obtained by the two methods is no evidence that the values are correct (as has been concluded by some investigators), for the agreement can be only an accidental one. Even the accidental very close agreement in the case of KCl at 0° disappears[4] at 25° when vapor pressure measurements are made the basis for calculating α. (Cf. XV, 2 and problem 4.)

Table XXIV

Comparison of the degrees of ionization calculated by the freezing-point method, equation (7, XIV), and by the conductance method, equation (12, XVII). α_F, by the freezing-point method. α_Λ, by the conductance method. [Cf. Jour. Amer. Chem. Soc., **33**, 1702 (1910).]

$\underline{N}_1$	Δt_F	$(1+\alpha_F)\underline{N}_1$	$100\alpha_F$	$100\alpha_\Lambda$
$CsNO_3$				
0.025	0.086^0	0.046	85.	89.1
0.10	0.325	0.175	75.	80.8
0.20	0.622	0.335	68.	74.6
0.50	1.419	0.770	54.	64.5
KCl				
0.025	0.089	0.947	92.	93.1
0.10	0.345	0.186	86.	87.9
0.20	0.680	0.367	84.	84.7
0.50	1.658	0.899	79.8	79.6
LiCl				
0.025	0.090	0.048	94.	90.7
0.10	0.351	0.189	89.	85.7
0.20	0.694	0.374	87.	82.3
0.50	1.791	0.924	84.8	78.0

6. The Influence of Ions upon the Thermodynamic Environment in Aqueous Solutions. (*a*) **Nature of the Influence.**—As stated above, the thermodynamic environment prevailing within a dilute solution of a strong electrolyte is quite appreciably different from that which prevails in pure water or in a dilute solution of a non-electrolyte, owing apparently to the comparatively great influence which the large numbers of electrically charged particles (the ions) exert upon the other molecular species in the solution with them. This influence manifests itself by its effect upon the tendencies of the various molecular species to escape from the solution into any other condition. (Cf. XII, 7, footnote 2.) Or, stated in other words, the fugacity (XIV, 1) of a given molecular species in a dilute aqueous solution is not simply a function of its own concentration but is a function of the ion concentration of the solution as well (XII, 9). The magnitude of the effect of the presence of the ions upon the fugacity of a given molecular species in the solution depends upon the nature of this species, and also, but frequently to a less degree, upon the nature of the ions present in the solution as well.

For the purpose of presenting the known facts concerning the effect of the ion concentration upon the fugacities of different species of solute molecules it will be convenient to divide these solute molecules into three classes, as follows: (1) the ions themselves; (2) the un-ionized molecules of strong electrolytes; and (3) all other neutral molecules.

It will be recalled that in a dilute solution of constant thermodynamic environment, in accordance with Henry's Law (equation 10, XIV), the fugacity of each species of solute molecule is proportional to its concentration, that is,

$$p_{\mathrm{A}} = k_{\mathrm{A}} C_{\mathrm{A}} \tag{14}$$

or

$$\frac{p_{\mathrm{A}}}{k_{\mathrm{A}} C_{\mathrm{A}}} = 1 \tag{15}$$

If therefore we plot values of the quantity $\frac{p_{\mathrm{A}}}{C_{\mathrm{A}}}$ —the *molal fugacity*—for each molecular species in a solution against corresponding values of the ion concentration of that solution, we shall obtain a picture of the effect of the changing thermodynamic environment upon the fugacity of each molecular species. Moreover the magnitude of the variation of the ratio, $\frac{p_A}{C_A}$, from constancy will be a measure of the sensitivity of the molecular species toward a variation of ion concentration in the medium surrounding it. As is evident from the form in which we are expressing Henry's Law, we shall confine the consideration to solutions so dilute that the mole fraction of each solute species is proportional to its volume concentration.

(*b*) **The Influence of the Ion Concentration upon the Fugacity of Ions.**—The nature of the influence is shown graphically in Fig. 31 in which the abscissæ represent total ion concentrations (*i.e.*, C_{K^+} or C_{Cl^-}) in solutions of KCl and the ordinates represent values of the ratio, $\frac{p_i}{C_i}$, for potassium- and chloride-ions in these solutions, calculated on the assumption that both ions behave alike and that the conductance ratio is a correct measure of the degree of ionization.[6] It will be noted that increasing the ion concentration of the solution causes the *molal fugacity*, $\frac{p_i}{C_i}$, of the ions to *decrease*, at first rapidly and then more slowly. Or, stated in another way, the more ions there are in the solution the less tendency they have to escape from the solution.

The total percentage change in the molal fugacity within the

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[6] The necessary data for calculating the variation of fugacity with ion concentration can be obtained by a variety of different methods. The measurement of any property of the solution which is thermodynamically connected with the fugacity of the solute species under consideration will furnish these data. The data employed in constructing the curves for the ions and un-ionized molecules of KCl, shown in Figs. 31 and 32 above, were (1) the partial osmotic pressures of these molecular species as computed by Bates (Jour. Amer. Chem. Soc., **37,** 1428 (1915)) from the freezing points of KCl solutions; and (2) the electromotive force of potassium chloride concentration cells as determined by MacInnes[a] and Parker (Ibid., **37,** 1456 (1915)). Either class of data alone suffices for constructing such a curve, and both sets of data for KCl were found to be in complete agreement with each other. The investigation of the solubility relations of thallous chloride in aqueous salt solutions also yields results very similar to those presented above. (See Bray, Jour. Amer. Chem. Soc., **33,** 1683 (1911).) Curve A in Fig. 32 is based upon the solubility of hydrogen gas in solutions of potassium chloride.

[a] Duncan Arthur MacInnes (1885–). Associate in Physical Chemistry at the University of Illinois.

range ($C_i = 0.001$ to 0.1) covered by the figure is less than 10 per cent., however, while within the range, $C_i = 0.005$ to 0.1, the percentage change is less than 3 per cent. For many purposes this comparatively small variation from constancy may be neglected and we may therefore formulate the following useful approximate principle: *In dilute aqueous solutions of electrolytes the fugacity of an ion-species is approximately proportional to its concentration.*

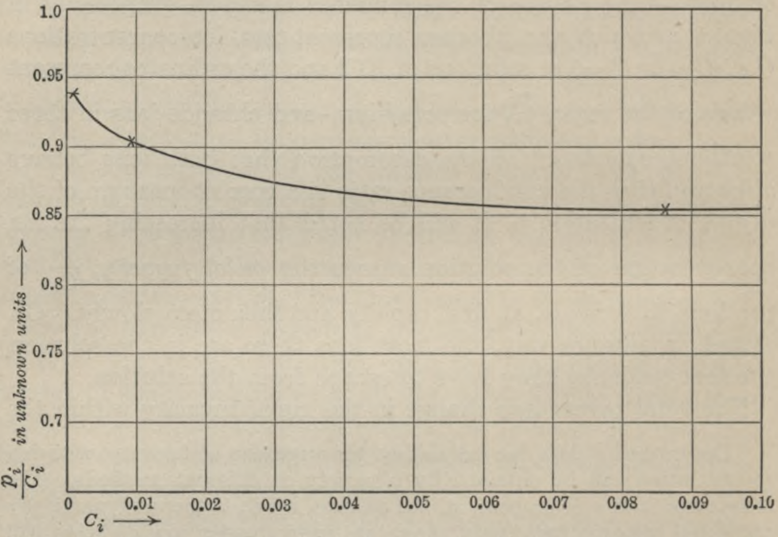

FIG. 31.—Illustrating the effect of varying ion concentration upon the fugacity of ions. The curve shown is for the ions of KCl.[6]

The curve shown in Fig. 31 can be satisfactorily represented by the following empirical equation:

$$\log_{10}\frac{p_i}{C_i} = k_i C_i^{h_i} + \text{const.} = -0.1157\,C_i^{0.207} + \text{const.} \qquad (16)$$

(*c*) **The Influence of the Ion Concentration upon the Fugacity of Un-ionized Molecules of Strong Electrolytes.**—This effect is shown graphically by curve *u* in Fig. 32, the values of the ordinates being indicated on the *left-hand* margin. The values employed are for the un-ionized molecules of KCl in solutions of this salt. It will be observed that the molal fugacity, $\frac{p_u}{C_u}$, of these molecules *increases* very rapidly with increasing ion concentration, the increase between $C_i = 0.001$ and $C_i = 0.1$ being about sevenfold. Stated in other terms, the presence of the ions in the solution *increases* the escaping tendency of the un-ionized molecules. This increase is known as the **salting-out effect.** It is shown generally by nearly all classes of neutral molecules when a salt is added to the solution containing them.

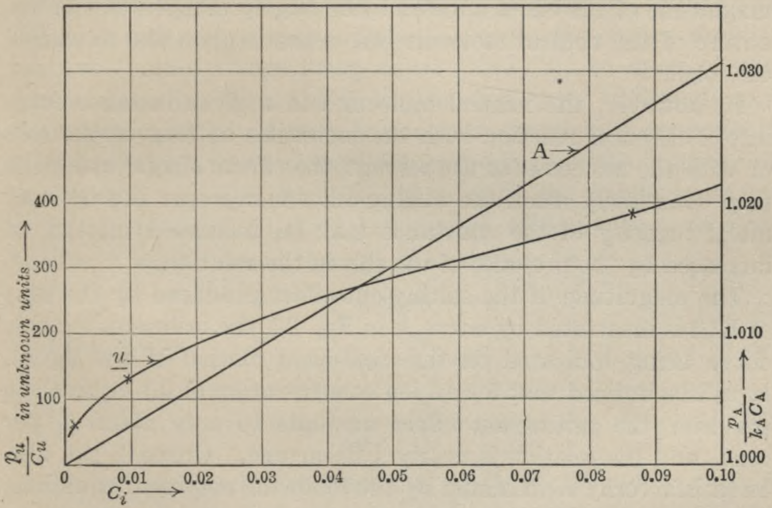

FIG. 32.—Illustrating the effect of varying ion concentration upon the fugacity of neutral molecules. Curve *u* is for the un-ionized molecules of KCl and curve A is for molecules of H_2, in solutions of KCl.[6]

The difference between the un-ionized molecules of strong electrolytes and other neutral molecules in this respect is that the magnitude of the salting-out effect is *very much greater* in the former case. As a partial explanation of this difference it has been suggested by A. A. Noyes that most of the un-ionized molecules of a strong electrolyte may be intra-molecularly polarized. A polarized molecule (Cf. I, 2*g*) of this character might well be more sensitive to changes in the ion concentration of the surrounding medium than would an unpolarized molecule.

This is also in accordance with the views of Sir J. J. Thomson (I, 2*g*).

Curve *u* in Fig. 32 can be satisfactorily represented by the empirical equation,

$$\log_{10}\frac{p_u}{C_u}=k_u C_i^{h_u}+\text{const.}=3.27C_i^{0.096}+\text{const.} \qquad (17)$$

(*d*) **The Effect of the Ion Concentration upon the Fugacity of Neutral Molecules in General.**—Neutral molecules in general undergo the salting-out effect in the presence of ions. The magnitude of the effect appears to be largely independent of the nature of the neutral molecule but depends upon the nature of the ions.

If, however, the neutral molecules in a given instance enter into a chemical reaction with the molecules or ions of the salt or with the molecules of the solvent, the effects of such reactions may completely mask the salting-out effect proper and the *total* molal fugacity of the substance may be decreased instead of increased by the presence of the salt in the solution.

The magnitude of the salting-out effect produced by the ions of KCl is illustrated by curve A in Fig. 32, the ordinates for this curve being indicated on the *right-hand* margin of the figure. It will be noticed that for an ion concentration of 0.1 equivalent per liter the salting-out effect amounts to only about 3 per cent., and the relation is nearly a linear one. Curve A can also be satisfactorily represented by the following empirical equation:

$$\log_{10}\frac{p_{\mathrm{A}}}{k_{\mathrm{A}}C_{\mathrm{A}}}=k'_{\mathrm{A}}C_i^{h}=0.13C_i \qquad (18)$$

REFERENCES

JOURNAL ARTICLES: (1) Washburn and Clark, Jour. Amer. Chem. Soc., **38** (1916). (2) Washburn, Ibid., **33**, 1461 (1911). (3) Harkins, Ibid., **33**, 1868 (1911). (4) Heuse, Univ. of Ill. Thesis, 1914, p. 20. (5) A. A. Noyes, Carnegie Inst. Pub. No. **63**, p. 339 (1907). (7) Lewis, Jour. Amer. Chem. Soc., **34**, 1643 (1915).

CHAPTER XVIII

ELECTRICAL TRANSFERENCE

1. The Phenomenon of Electrical Transference.—We have seen (XVI, 3) that when a current of electricity is passed through a solution of an electrolyte *all* of the anions move toward the anode and *all* of the cations toward the cathode. Since the different ions move with different speeds, the faster moving ones will, other things being equal (XVI, 3), do more of the current-carrying than the slower moving ones. Through any cross section of the solution, however, the number of equivalents of cation which move toward the cathode plus the number of equivalents of anion which move toward the anode must by definition be equal to the total number of equivalents of electricity (XVI, 5) passed through the solution, or

$$N_c+N_a=N_e \tag{1}$$

and the ratios

$$\frac{N_c}{N_c+N_a}=\frac{N_c}{N_e}=n_c \tag{2}$$

and

$$\frac{N_a}{N_c+N_a}=\frac{N_a}{N_e}=n_a \tag{3}$$

evidently represent the fractional part of the total current carried by each species of ion and also the number of equivalents of each ion species as well as the number of equivalents of each ion-constituent *transferred* in the one direction or the other through the solution during the passage of one faraday of electricity. The quantities n_c and n_a are called the **transference numbers** (XVII, 2*b*) of the ions and of the ion-constituents indicated by the subscripts. As a result of this transfer of ions through the solution, concentration changes take place around the electrodes. The nature of these changes and their relation to the transference number may be best understood by the consideration of a Hittorf[a] transference experiment.

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[a] Johann Wilhelm Hittorf (1824–1914). Professor of Physics in the University of Münster, Germany.

2. A Hittorf Transference Experiment.—Let a solution of silver nitrate be electrolyzed between silver electrodes in the apparatus shown diagrammatically in Fig. 33. At the end of the electrolysis let the solution be drawn off in five separate portions, three middle portions and two electrode portions, as indicated in the figure, precautions being taken to prevent mixing during this operation. Let each portion be weighed and analyzed to determine the per cent. of water and the per cent. of silver nitrate which it contains. The result of these analyses will show that the three middle portions have the same composition as the original solution (if the experiment has been properly conducted), but that the concentration of silver nitrate has increased in the anode portion and decreased in the cathode portion. The mechanism of these concentration changes is the following:

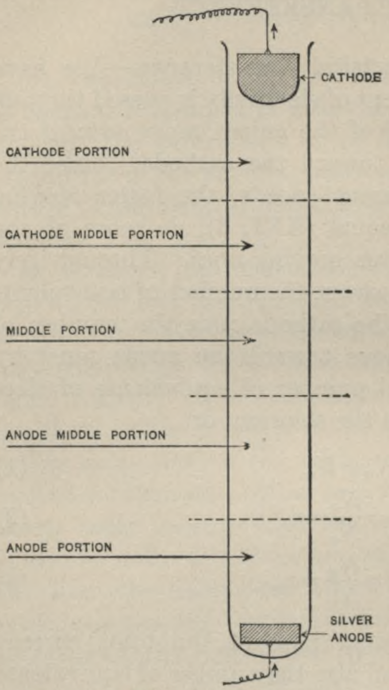

Fig. 33.—Diagrammatic representation of a transference apparatus showing division into portions for analysis.

At the anode, in accordance with Faraday's Law, N_e equivalents of silver have dissolved from the electrode and passed into solution as silver ion (XVI, 4*a*), N_e being the number of equivalents of electricity passed through the solution during the experiment. At the same time a certain amount, N_c equivalents, of silver ion has moved *out of* the anode portion, and $N_e - N_c$ equivalents of nitrate ion have moved *into* the anode portion. (See equation 1.) Suppose that the analysis of the anode portion gives the composition N_2 equivalents of $AgNO_3$ in m_w grams of water. The original solution before electrolysis contained N_1 equivalents of $AgNO_3$ in m_w grams of water. The *increase*, $N_2 - N_1$, must evidently be equal to $N_e - N_c$, that is, it must be equal to the silver which has come into the anode portion from the electrode diminished by the silver which has gone out of the anode portion owing to the migration of silver ions toward the cathode. Hence by definition (equation 2), the transference number of the silver ion is evidently

$$n_c = \frac{N_c}{N_e} = \frac{N_1 - N_2 + N_e}{N_e} \tag{4}$$

and that of the nitrate ion is by definition (equations 2 and 3), $n_a = 1 - n_c$. At the cathode the reverse of the above process takes place and from the analysis of the cathode portion the two transference numbers can also be calculated by means of equation (4), thus giving a valuable check on the accuracy of the experimental work.

In employing equation (4) the following points, which follow from its derivation, should be kept clearly in mind: From the total mass and composition of the electrode portion as calculated from the results of the analysis and the knowledge of the electrode process, the mass of water, m_w, in the electrode portion can be computed. The analysis also gives the number of equivalents, N_2, of the ion-constituent whose transference number is desired, which are present in the m_w grams of water in the electrode portion. From the known composition of the original solution we can calculate the number of equivalents, N_1, of this ion-constituent which were present in m_w grams of water in the original solution. N_e *in the numerator* of equation (4) is the number of equivalents of the ion-constituent in question which have passed *into* the electrode portion *from the electrode.* If the ion-constituent happens to have gone *out of* the solution *on to* the electrode, then N_e is obviously a negative quantity. In many cases it will be zero. N_e *in the denominator* of equation (4) is the number of equivalents of electricity passed through the solution during the experiment, as measured by a suitable coulometer (XVI, 5) connected in series with the transference apparatus.

3. True Transference Numbers and Ionic Hydration.—It will be noted that the above calculation of transference numbers by the Hittorf method assumes that all of the water in the solution remains stationary during the passage of the current, and the change in composition which occurs in the neighborhood of the electrode is calculated with reference to the water, assumed to be stationary. The assumption is not strictly true, since the ions are hydrated (XV, 1) and hence some water is also carried with them as they move through the solution. In dilute solution the water so carried is negligible, but in concentrated solution it is not and it becomes necessary to add to the solution a third substance, such as sugar, which will remain stationary during the passage of the current and which can serve as the reference substance for measuring the concentration changes of the salt and the water. In this way the comparative degrees of hydration of different ions have been measured.

TABLE XXV

Ionic hydrations and "true" transference numbers at 25° obtained from transference experiments in the presence of a non-electrolyte as a reference substance. n_c^{T} = true transference number of the cation, n_∞ = transference number at infinite dilution, n_c^{H} = Hittorf transference number at $1.3n$, Δn_w = number of moles of water transferred from anode to cathode per faraday, N_w = number of water molecules attached to an ion. (See Jour. Amer. Chem. Soc., **37**, 698 (1915).)

Electrolyte (Conc. $1.3n$)	$\Delta n_w / n_c^{T}$	Δn_w	n_c^{T}	n_∞	n_c^{H}
HCl.........	0.28 ± 0.04	0.24 ± 0.04	0.844	0.833	0.82
CsCl........	0.67 ± 0.1	0.33 ± 0.06	0.491	0.491	0.485
KCl.........	1.3 ± 0.2	0.60 ± 0.08	0.495	0.495	0.482
NaCl........	2.0 ± 0.2	0.76 ± 0.08	0.383	0.396	0.366
LiCl........	4.7 ± 0.4	1.5 ± 0.1	0.304	0.330	0.278

$$N_w^{H} = 0.28 \pm 0.04 + 0.185 N_w^{Cl} \tag{1}$$
$$N_w^{Cs} = 0.67 \pm 0.1 + 1.03\ N_w^{Cl} \tag{2}$$
$$N_w^{K} = 1.3 \pm 0.2 + 1.02\ N_w^{Cl} \tag{3}$$
$$N_w^{Na} = 2.0 \pm 0.2 + 1.61\ N_w^{Cl} \tag{4}$$
$$N_w^{Li} = 4.7 \pm 0.4 + 2.29\ N_w^{Cl} \tag{5}$$

Transference numbers obtained by using a reference substance which remains stationary during the passage of the current are called "true" transference numbers, while those obtained by the use of water as the reference substance are called "Hittorf" transference numbers. In dilute solution, however, the two become practically identical as is evident from the following relation which connects them

$$n_a^{\mathrm{T}} = n_a^{\mathrm{H}} - \Delta n_w \frac{N_s}{N_w} \qquad (5)$$

n_a^{T} and n_a^{H} are respectively the true and the Hittorf transference numbers, Δn_w is the number of moles of H_2O transferred from anode to cathode per faraday of electricity and $\frac{N_s}{N_w}$ is the molal ratio, $\frac{\text{electrolyte}}{H_2O}$, in the original solution. The relative ionic hydrations and true transference numbers obtained in this way in the case of the uni-univalent chlorides are shown in Table XXV.

Note.—Compare the relative degrees of hydration of the alkali ions as shown in Table XXV with their ion-conductances given in Table XXI and with the atomic weights of the elements, Table I.

4. Change of Transference Numbers with Concentration and Temperature.—In the case of uni-univalent salts the transference numbers change very little with the concentration as long as the latter does not exceed a moderate value, say 0.01 normal. This is illustrated by the following values of n_c (Hittorf) at 18°.

Values of n_c^{H} at 18°

C	0.0	0.005	0.01	0.02	0.05	0.1	0.2	0.3	0.5	1.0
KCl.......	0.496	0.496	0.496	0.496	0.496	0.495	0.494	.....	.....	.....
NaCl......	0.398	0.396	0.396	0.396	0.395	0.393	0.390	0.388	0.382	0.369
LiCl.......	0.338	.....	0.332	0.328	0.320	0.313	0.304	0.299	.....	.....

With rising temperature all transference numbers which have been measured exhibit a tendency to approach 0.5.

For compiled tables of the best transference data see reference (1).

Problem 1.—If the anion transference number of potassium chloride is 0.504 and if the equivalent conductance at infinite dilution has the following values: 129.5 for KCl, 125.9 for KNO_3, and 104.9 for $NaNO_3$, what is the transference number of sodium nitrate?

5. Transference and Ion Mobility.[1]—A charged body in an electric field is acted upon by a force, f, equal to the product of the charge, q, into the potential gradient (dE/dl) at that point in the field, or

$$f = q(dE/dl) \qquad (6)$$

where $\mathrm{d}E$ is the change in potential in the distance $\mathrm{d}l$. Moreover, the velocity of a small body moving through a medium of great frictional resistance is proportional to the force acting upon it. Hence the velocity, u, with which an ion moves through a solution of a given viscosity is proportional to the potential gradient prevailing within the solution (q being obviously a constant for a given ion), that is,

$$u_{c+} = U_{c+}(\mathrm{d}E/\mathrm{d}l) \text{ and } u_{a-} = U_{a-}(\mathrm{d}E/\mathrm{d}l) \qquad (7)$$

where the proportionality factor (U_{c+}, U_{a-}) is obviously the velocity of the ion under unit potential gradient. It is called the **mobility** of the ion and is a characteristic property which varies with the temperature and with the nature of the medium through which the ion moves. Similarly the velocity with which a given *ion-constituent* is transferred through the solution will be

$$u_c = \alpha U_{c+}(\mathrm{d}E/\mathrm{d}l) = U_c(\mathrm{d}E/\mathrm{d}l) \qquad (8)$$

and similarly for the anion

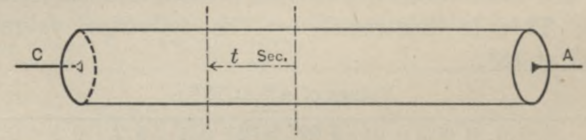

FIG. 34.

If a constant current, I, of electricity be passed for t seconds through a solution containing C equivalents of a uni-univalent electrolyte, CA, per liter, placed in a cylindrical tube of cross section A, between parallel electrodes 1 cm. apart, a consideration of Fig. 34 will show that the number of equivalents, N_c, of the cation-constituent which pass through any cross section of the tube in this time will be

$$N_c = u_c tA(0.001C) \qquad (9)$$

or, since $u_c = U_c(\mathrm{d}E/\mathrm{d}l)$, by equation (8), and $\mathrm{d}E/\mathrm{d}l$ equals E/l for a constant current in a homogeneous conductor of uniform cross section (prove this, see equations (25) and (27), XVI), equation (9) becomes

$$N_c = U_c(E/l)tA(0.001C) \qquad (10)$$

and similarly for the number of equivalents of anion-constituent passing in the opposite direction,

$$N_a = U_a(E/l)tA(0.001C) \tag{11}$$

If we divide each of these equations by their sum we obtain an expression for each of the transference numbers (see equations 2 and 3) in terms of the mobilities of the ion-constituents.

$$n_c = \frac{U_c}{U_c + U_a} \text{ and } n_a = \frac{U_a}{U_c + U_a} \tag{12}$$

6. Transference and Ion-Conductances.—In the example just considered (Fig. 34), the total number of coulombs, q, of electricity passed through our solution in the time t is by definition (equation (24), XVI)

$$q = It \tag{13}$$

By Faraday's Law (equation (23), XVI), it is also

$$q = FN_e \tag{14}$$

and N_e the number of equivalents of electricity passed is, according to equation (1), expressed by the sum of equations (10) and (11), thus giving us

$$It = q = FN_e = F(N_c + N_a) = F(U_c + U_a)\,(E/l)tA(0.001C) \tag{15}$$

By simply combining this equation algebraically with equations (25, 26, 27 and 29, XVI) (prove this), we obtain the important relation,

$$\Lambda = F(U_c + U_a) = FU_c + FU_a \tag{16}$$

and hence

$$\Lambda = F\alpha U_{c+} + F\alpha U_{c-} \tag{17}$$

or in words, the equivalent conductance of a uni-univalent electrolyte is equal to the faraday multiplied either by the sum of the mobilities of its ion-constituents or by the product of the degree of ionization into the sum of the mobilities of its ions. But the equivalent conductance of the salt is equal to the sum of the equivalent conductances of its two ion-constituents, or to the product of its degree of ionization into the sum of the conductances of its two ions (XVII, 2, equations 2, 3, and 4), that is,

$$\Lambda = \Lambda_c + \Lambda_a \tag{18}$$

and

$$\Lambda = \alpha(\Lambda_{c^+} + \Lambda_{a^-}) \tag{19}$$

and by comparing these two equations with equations (16) and (17), it is evident that

$$\Lambda_c = FU_c,\ \Lambda_a = FU_a \tag{20}$$

and

$$\Lambda_{c^+} = FU_{c^+},\ \Lambda_{a^-} = FU_{a^-} \tag{21}$$

and the absolute velocity in centimeters per second with which a given ion (or ion-constituent) moves through a solution under unit potential gradient is evidently equal to the equivalent conductance of the ion (or ion-constituent) in the solution in question, divided by the faraday.

Equations (12) and (16) combined with (20) and (21) give

$$\Lambda_c = \Lambda n_c,\ \Lambda_a = \Lambda n_a \tag{22}$$

and

$$\Lambda_{c^+} = \alpha \Lambda n_c,\ \Lambda_{a^-} = \alpha \Lambda n_a \tag{23}$$

both of which at infinite dilution become (since $\alpha = 1$)

$$\Lambda_{0c} = \Lambda_{0c^+} = \Lambda_0 n_c, \text{ and } \Lambda_{0a} = \Lambda_{0a^-} = \Lambda_0 n_a \tag{24}$$

We have seen how values of Λ_0 and of n are obtained experimentally (XVII, 1, and XVIII, 2 and 7), and it is clear that by means of equation (24) the individual ion-conductances at infinite dilution recorded in Table XXI can be computed. To compute such a table all that is necessary is a set of Λ_0 values for a sufficient number of electrolytes to include all of the desired ion species and the transference number of a single ion species of one of those electrolytes in very dilute solution. The values given in Table XXI are based upon the transference number of potassium chloride. (See Sec. 4.)

Problem 2.—A transference experiment is made with a solution of silver nitrate (0.00739 gram of silver nitrate per gram of water) using two silver electrodes. A silver coulometer in the circuit shows a deposit of 0.0780 gram of silver. At the end of the experiment the anode portion weighing 23.38 grams is removed and found on analysis to contain 0.2361 gram of silver nitrate. Calculate the transference numbers of the silver and nitrate ions in a silver nitrate solution of this concentration. The cathode portion weighs 25.00 grams. How much silver nitrate does it contain?

7. Determination of Transference Numbers by the Moving Boundary Method.—From equations (7) and (12) it is evident that the ratio of the transference numbers of the two ions in a given salt solution is equal to the ratio of the velocities with which the two ion-constituents move through the solution and hence equal to the ratio of the distances covered by the two ion-constituents in a given time during the passage of the current. These two distances can be directly measured with the apparatus shown diagrammatically in Fig. 35. A solution of the salt, CA, under investigation is placed between one of the salt CA′ and another of the salt C′A, having respectively the same cation and anion as the salt CA. The boundaries *aa* and *bb* separating the solutions are easily visible because of the different refractive indices (VIII, 3) of the solutions. A current is passed through the apparatus in the direction indicated by the short arrows. Boundary *aa* moves upward to *a′a′* and evidently represents the distance covered by the anion-constituent A during the passage of the current. Similarly boundary *bb* moves downward to *b′b′* and represents the distance covered by the cation-constituent. The ratio of the two distances is the ratio of the two transference numbers.

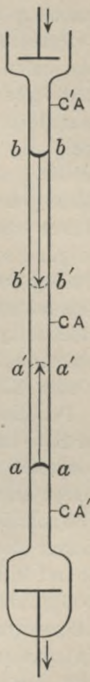

Fig. 35.

Problem 3.—Prove that the two boundaries will remain sharp while the current passes, if $U_{a'} < U_a$ and $U_{c'} < U_c$. The salts are so chosen that these conditions are fulfilled. If one desired to measure the transference number of NaCl by this method, what salts might be used for C′A and CA′?

The experimental development of the moving boundary method has been due chiefly to Denison[a] and Steele.[2] When employed in practice it is necessary, as shown by Lewis,[3] to correct the measured distance covered by the moving boundary for any mass displacement of the solution due to electrode processes. When so corrected the transference number yielded by this method has been shown by Miller[4,b] and by Lewis[3] to be identical with the Hittorf number.

[a] Robert Beckett Denison. Professor of Chemistry in Natal University College, Pietermaritzburg, S. Africa.

[b] William Lash Miller (1866–). Professor of Physical Chemistry in the University of Toronto.

PROBLEMS

The atomic weight table and the values of general constants such as the faraday may be employed in solving the following problems but no other data except those given with the problem are to be used. The influence of viscosity may be neglected in computing α.

Problem 4.—Using a silver anode and a silver chloride cathode, 0.04974 equivalent of electricity was passed through an aqueous solution containing 8.108 per cent. of KCl and 4.418 per cent. of raffinose contained in a suitable transference apparatus. At the end of the experiment the anode portion weighing 103.21 grams was analyzed and found to contain 6.510 per cent. of KCl and 4.516 per cent. of raffinose. The cathode portion weighing 85.28 grams contained 10.030 per cent. of KCl and 4.290 per cent. of raffinose. Three middle portions were found to have the same composition as the original solution. On the assumption that the raffinose remains stationary during the passage of the current calculate the true transference number of the potassium ion and the amount of water transferred per equivalent of electricity. Assuming that N_w^{Cl} molecules of water are attached to the chloride ion calculate the number attached to the potassium ion. (Cf. Table XXV.)

Problem 5.—A solution containing 0.1 equivalent of KCl per 1000 grams of H_2O has a specific resistance of 89.37 ohms at 18° and is 86.15 per cent. ionized. This solution is electrolyzed in a transference apparatus with a silver anode and a silver chloride cathode. At the end of the electrolysis the solution around each electrode is neutral and no gas has been evolved at either electrode. The anode is carefully washed, dried and weighed and is found to have increased in weight by 0.01300 gram. A cathode portion of 100 grams is drawn off from the neighborhood of the cathode and is found on analysis to contain 0.7539 gram of KCl. Calculate from these data (*a*) the equivalent conductance of potassium ion at infinite dilution, (*b*) the absolute velocity in centimeters per second of chloride ion in dilute solution at 18° when moving under a potential gradient of 2 volts per centimeter, and (*c*) the absolute velocity of chloride ion-constituent under the same conditions.

Problem 6.—The specific conductance of 0.01 normal potassium nitrate solution at 18° is 0.001182 mho. Its equivalent conductance at infinite dilution at the same temperature is 125.9 mhos. Calculate its degree of ionization. On the assumption that it has the same degree of ionization at 0°, calculate approximately its freezing point.

Problem 7.—The equivalent conductance of silver nitrate at infinite dilution is 115.7 mhos at 18°. From the result obtained in problem 2, calculate the equivalent conductances of the silver and nitrate ions at infinite dilution.

Problem 8.—From the result obtained in problem 7, together with the data given in problem 6, calculate the equivalent conductance of infinitely dilute potassium chloride solution at 18°, the equivalent conductance of silver chloride at infinite dilution being 119.3 mhos.

Problem 9.—From the result obtained in problem 8, calculate approximately the specific conductance of 0.05 normal potassium chloride solution at 18°. The freezing point of this solution is −0.175°. Assume the same degree of ionization at 0° and 18°.

Problem 10.—Calculate approximately the conductance of 0.1 normal sodium nitrate solution at 18° in the cell of problem 11. The freezing point of the solution is −0.338° and its equivalent conductance (18°) at infinite dilution is 104.9 mhos.

Problem 11.—A cylindrical conductivity cell of 1 cm. radius is fitted tightly with parallel silver electrodes 2 cm. apart and is filled with a 0.1*n* solution of $AgNO_3$ for which the transference number of the positive ion is 0.468. A potential difference of 6.750 volts causes a current of 0.1 ampere to flow through the cell. The equivalent conductance of KNO_3 at infinite dilution is 125.9 mhos and the transference number of the positive ion is 0.511. Calculate the degree of ionization of $AgNO_3$ in 0.1*n* solution.

Problem 12.—Calculate the degree of ionization of ammonium hydroxide in 0.1 normal solution from the following data: its equivalent conductance at 25° in 0.1 normal solution is 4; the equivalent conductance of ammonium chloride at infinite dilution is 155, the transference number for the positive ion is 0.50 in the case of ammonium chloride and 0.27 in the case of ammonium hydroxide.

Problem 13.—Describe with sketch of apparatus an experiment by means of which one could determine, more definitely than from the data in problem 5, XV, the nature of the complex formed between NH_3 and $AgNO_3$ in solution.

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CHAPTER XIX

THERMOCHEMISTRY

1. Heat of Reaction.—It may be stated as a general rule that all physical and chemical reactions are accompanied by heat effects. The **heat of reaction** is defined to be the number of calories of heat *evolved* when the reaction takes place, *at constant volume* in the direction indicated, and between the amounts of the reacting substances indicated, by the stoichiometrical equation of the reaction. Thus the equation

$$2\overline{H}_2+\overline{O}_2=2\overline{H_2O}+117{,}400 \tag{1}$$

signifies that when 4 grams of hydrogen gas unite in a closed vessel with 32 grams of oxygen gas to form 36 grams of water vapor, 117,400 cal. of heat are *evolved*. The **thermochemical equation** of this reaction might, if desired, be written,

$$\overline{H}+\tfrac{1}{2}\overline{O}=\tfrac{1}{2}\overline{H_2O}+29{,}350 \tag{2}$$

which is the thermochemical equation for the union of 1 gram of gaseous hydrogen with 8 grams of gaseous oxygen to form 9 grams of water vapor. A horizontal line *above* the formula of a substance in a thermochemical equation indicates that the substance is understood to be in the gaseous state. Similarly the *absence* of any line indicates the liquid state, a line *below* the formula indicates the crystalline state, and a suffix, *aq* (thus HCl*aq*), indicates that the substance is in solution in such a large volume of water that the addition of more water would not produce any appreciable heat effect, that is, the solution is understood to be so dilute that its **heat of dilution** is negligibly small.

Problem 1.—State in words the significance of the following thermochemical equations. The values given are all for room temperature (18°).

$$\underline{C}+\overline{O}_2=\overline{CO}_2+94{,}310 \tag{3}$$

$$\overline{CO}+\overline{O}=\overline{CO}_2+68{,}000 \tag{4}$$

$$\underline{CaO}+2HCl\,aq=CaCl_2\,aq+H_2O+46{,}200 \tag{5}$$

$$\underline{\mathrm{Zn}}+\mathrm{H_2SO_4}aq=\mathrm{ZnSO_4}aq+\overline{\mathrm{H}}_2+37{,}700 \tag{6}$$

$$\underline{\mathrm{Ca}}+\underline{\mathrm{H_2O}}=\underline{\mathrm{CaO}}+\mathrm{H_2}+81{,}000 \tag{7}$$

$$\underline{\mathrm{Ca}}+2\mathrm{H_2O}=\underline{\mathrm{Ca(OH)}}_2+\overline{\mathrm{H}}_2+143{,}700 \tag{8}$$

$$\underline{\mathrm{Ca}}+2\mathrm{H_2O}+aq=\mathrm{Ca(OH)_2}aq+\overline{\mathrm{H}}_2+94{,}100 \tag{9}$$

$$\mathrm{AgNO_3}aq+\mathrm{KCl}aq=\underline{\mathrm{AgCl}}+\mathrm{KNO_3}aq+15{,}800 \tag{10}$$

$$\underline{\mathrm{KCl}}+aq=\mathrm{KCl}aq-4400 \tag{11}$$

$$\underline{\mathrm{H_2O}}=\mathrm{H_2O}-1450\ (\text{at } 18^\circ) \tag{12}$$

$$\mathrm{H_2O}=\overline{\mathrm{H_2O}}-9990\ (\text{at } 18^\circ) \tag{13}$$

$$\underline{\mathrm{C_{12}H_{22}O_{11}}}+12\overline{\mathrm{O}}_2=12\overline{\mathrm{CO}}_2+11\overline{\mathrm{H_2O}}+1{,}243{,}000 \tag{14}$$

$$\mathrm{C_6H_6}+7\tfrac{1}{2}\overline{\mathrm{O}}_2=6\overline{\mathrm{CO}}_2+3\overline{\mathrm{H_2O}}+754{,}300 \tag{15}$$

2. Hess's Law.—

Problem 2.—By means of the First Law of thermodynamics (X, 4) prove (1) that the heat of a given reaction is independent of whether the reaction actually takes place as written or whether it occurs in stages, and (2) if it occurs in stages, that the heat of the reaction is independent of what the stages are and in what order they may occur.

These facts were discovered by Hess[a] in 1840 before the First Law of thermodynamics had been established as a general principle. They may be illustrated by the process of forming a dilute solution of NH_4Cl from $\overline{NH}_3$ and $\overline{HCl}$. This process may take place in two different ways, thus:

$$(1)\ \overline{\mathrm{NH}}_3+\overline{\mathrm{HCl}}=\underline{\mathrm{NH_4Cl}}+42{,}100 \tag{16}$$

and

$$\underline{\mathrm{NH_4Cl}}+aq=\mathrm{NH_4Cl}aq-3900 \tag{17}$$

equals

$$\overline{\mathrm{NH}}_3+\overline{\mathrm{HCl}}+aq=\mathrm{NH_4Cl}aq+38{,}200 \tag{18}$$

$$(2)\ \overline{\mathrm{NH}}_3+aq=\mathrm{NH_3}aq+8400 \tag{19}$$

and

$$\overline{\mathrm{HCl}}+aq=\mathrm{HCl}aq+17{,}300 \tag{20}$$

and

$$\mathrm{HCl}aq+\mathrm{NH_3}aq=\mathrm{NH_4Cl}aq+12{,}300 \tag{21}$$

equals

$$\overline{\mathrm{NH}}_3+\overline{\mathrm{HCl}}+aq=\mathrm{NH_4Cl}aq+38{,}000 \tag*{(18)}$$

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[a] Germain Henry (Hermann) Hess (1802–1850). Professor of Chemistry in the University of St. Petersburg.

It is evident from these reactions that the heat of the whole reaction,

$$\overline{NH_3}+\overline{HCl}+aq=NH_4Cl\,aq \tag{22}$$

is, within the experimental error (200 cal.), the same in both cases.

Thermochemical equations can be added and subtracted, or multiplied and divided just the same as algebraic equations. Hess's Law is of great practical importance in computing the heat of reaction for cases where it cannot be directly measured. A large part of the thermochemical data available at the present time[1] is the result of the pioneer investigations of Thomsen[a] and of Berthelot.[b]

Problem 3.—From the thermochemical equations given in this chapter calculate the heats of the following reactions:

$$\underline{C}+\overline{O}=\overline{CO}+? \tag{23}$$

$$\underline{Ca(OH)_2}+aq=Ca(OH)_2aq+? \tag{24}$$

$$Ca(OH)_2aq+2HCl\,aq=CaCl_2aq+2H_2O+? \tag{25}$$

$$\overline{H}_2+\overline{O}=H_2O+? \tag{26}$$

3. Heat of Formation.—The heat of formation of a compound is the heat of the reaction by which the compound is formed out of its elements. Thus the heat of formation of cane sugar, $C_{12}H_{22}O_{11}$, out of solid carbon and gaseous oxygen and hydrogen would be the heat of the reaction

$$12\underline{C}+22\overline{H}+11\overline{O}=\underline{C_{12}H_{22}O_{11}}+? \tag{27}$$

Problem 4.—Compute the heat of this reaction from the reactions given above. Compute also the heat of formation of liquid benzene, C_6H_6, from its elements. From these two examples formulate a general rule for calculating the heat of formation of a compound of C, H and O, from its heat of

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[a] (Hans Peter Jürgen) Julius Thomsen (1826–1908). Professor of Chemistry in the University of Copenhagen. The results of his exhaustive thermochemical studies are embodied in his *Thermochemische Untersuchungen.*

[b] (Pierre Eugène) Marcellin Berthelot (1827–1907). The son of a physician. Professor of Chemistry, first at the École Supériore de Pharmacie, and after 1865 at the Collège de France. His extensive researches in chemical equilibrium and thermochemistry are embodied in his *Mechanique Chimique* published in 1879. He is buried in the Panthéon.

combustion. Heats of combustion are comparatively easy to measure and through them it is possible to calculate the heats of many other reactions which cannot be directly measured.

Problem 5.—From the heats of combustion of ethyl alcohol and acetic acid, respectively,

$$C_2H_5OH+6\overline{O}=2\overline{CO_2}+3H_2O+325{,}700 \qquad (28)$$

$$CH_3COOH+4\overline{O}=2\overline{CO_2}+2H_2O+209{,}400 \qquad (29)$$

calculate the heat of the reaction

$$C_2H_5OH+\overline{O}_2=CH_3COOH+H_2O+?$$

4. Heats of Precipitation and of Neutralization.—

Problem 6.—The following thermochemical equations are true (Ac = the acetate radical, CH_3COO):

$$HCl\,aq+AgNO_3\,aq=\underline{AgCl}+HNO_3\,aq+15{,}800 \qquad (30)$$

$$KCl\,aq+AgNO_3\,aq=\underline{AgCl}+KNO_3\,aq+15{,}800 \qquad (31)$$

$$NaCl\,aq+\tfrac{1}{2}Ag_2SO_4\,aq=\underline{AgCl}+\tfrac{1}{2}Na_2SO_4\,aq+15{,}800 \qquad (32)$$

$$\tfrac{1}{2}BaCl_2\,aq+AgClO_3\,aq=\underline{AgCl}+\tfrac{1}{2}Ba(ClO_3)_2\,aq+15{,}800 \qquad (33)$$

$$CsCl\,aq+AgAc\,aq=\underline{AgCl}+CsAc\,aq+15{,}800 \qquad (34)$$

Explain in terms of the Ionic Theory why the heat of reaction is the same for all of the above reactions.

Problem 7.—The heat of neutralization of HCl by NaOH in dilute solution is expressed by the thermochemical equation

$$HCl\,aq+NaOH\,aq=NaCl\,aq+H_2O+13{,}700 \qquad (35)$$

By means of the Ionic Theory predict the heat of the following reaction,

$$LiOH\,aq+HNO_3\,aq=LiNO_3\,aq+H_2O+?$$

Problem 8.—When 10 liters of $0.1n$ HCl are mixed with 10 liters of $0.1n$ NaAc (both at 18°), the temperature of the mixture rises 0.0150°. On the assumption that the specific heat capacity (X, 2) of the solution is equal to unity, calculate the heat of the reaction. What is the heat of neutralization of NaOH by HAc in $0.1n$ solution?

(Suggestion: Write all reactions in the ionic form *as regards the strong electrolytes* (Cf. XVII, 3).)

5. Heat Effects at Constant Volume and at Constant Pressure.

—When a reaction takes place at constant volume, the *heat effect* (H_v, cal. evolved) which accompanies it is by definition understood to be the heat-of-the-reaction (XIX, 1). When a reaction occurs without change of volume there is evidently no work performed against the external pressure, and hence by the First Law of thermodynamics (X, 3),

$$H_v = -\Delta U \tag{36}$$

If, however, the reaction occurs at constant pressure P, and is accompanied by an increase of volume Δv, then according to the First Law, the heat effect (H_p, cal. evolved) at constant pressure differs from that at constant volume simply by the work $P\Delta v$, performed *by* the system in the second case (X, 3 and 4, equation 3), that is,

$$H_v - H_p = P\Delta v \tag{37}$$

In the case of liquid or crystalline systems, Δv is always small, and hence in most cases $P\Delta v$ is negligible and for practical purposes we may assume

$$H_v = H_p \tag{38}$$

but when gases are involved in the reaction, Δv is frequently large and the work term must be taken into account.

Problem 9.—If A, B, M and N are perfect gases, show that for the reaction, $a\overline{\mathrm{A}} + b\overline{\mathrm{B}} = m\overline{\mathrm{M}} + n\overline{\mathrm{N}}$ occurring at constant pressure P, and constant temperature T, the work performed against the external pressure will be

$$P\Delta v = (m+n-a-b)RT \tag{39}$$

and hence

$$H_v - H_p = (m+n-a-b)RT \tag{40}$$

Problem 10.—Calculate in calories the difference between H_v and H_p for the following reactions: (1) $2\overline{H_2} + \overline{O_2} = 2\overline{H_2O}$ at 20°; (2) $\underline{C} + \overline{O_2} = \overline{CO_2}$ at 2000°; (3) $H_2O = \overline{H_2O}$ at 5°; (4) $\underline{H_2O} = H_2O$ at 0° and 1 atm. The density of ice is 0.9 gram per cubic centimeter.

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CHAPTER XX

THE HEAT CAPACITY AND INTERNAL ENERGY OF MATERIAL SYSTEMS[1]

GENERAL

1. Heat Capacity at Constant Volume and at Constant Pressure.—When a substance is heated at constant volume, no external work is performed during the heating, but when the heating takes place at constant pressure, the substance expands and hence does a certain amount of work both against the external pressure (X, 5) and against the internal attractive forces. The amounts of heat required in the two cases will, according to the First Law of Thermodynamics (X, 4), differ from each other simply by the amount of external work done in the second case plus the change in internal energy which accompanies the volume increase; and the following relation connecting the specific heat capacity (definition, X, 2; frequently shortened to "specific heat") at constant volume, $c_v(=\left(\frac{\partial Q}{\partial T}\right)_v)$, with that at constant pressure, $c_p(=\left(\frac{\partial Q}{\partial T}\right)_p)$, is readily deducible from the two laws of thermodynamics (see Appendix, 17):

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \tag{1a}$$

which may also be written

$$c_p - c_v = \frac{T\alpha^2}{\beta D} \tag{1b}$$

where $\alpha(=\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p)$ is the coefficient of cubical expansion, $\beta(=-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T)$ the coefficient of compressibility, and D the density of the substance per cubic centimeter, all at the absolute temperature T. The specific heat capacity at constant pressure is ordinarily the only one which can be conveniently determined calorimetrically, and hence equation (1) is especially important because it makes possible the exact calculation of the value for constant volume. The product of the specific heat capacity into the molal or atomic weight is called the **molal** or **atomic heat capacity** and will be designated similarly by the symbols C_p and C_v.

For *moderate and low temperatures* Nernst and Lindemann[a] find[4] that the following approximation form of equation (1*b*) is sufficiently exact for *solid substances:*

$$C_p = C_v + AC_v^2T \tag{2}$$

where A is a constant, characteristic of the substance and independent of T and which can therefore be evaluated from any pair of values of C_p and C_v. The constant A is also approximately equal to $\frac{0.0214}{T_F}$, where T_F is the absolute melting point of the substance.

Problem 1.—For aluminium at 0° the following values have been obtained: $c_p = 0.2079$ cal., $\alpha = 68.4 \cdot 10^{-6}$ per deg., $\beta = 1.3 \cdot 10^{-6}$ per megabar, and $D = 2.7$ grams per c.c. Calculate c_v in cal. at 0°. Calculate also the difference, $c_p - c_v$, at $-190°$. (NOTE: The **bar** is the unit of pressure in the absolute system; mega $= 10^6$. Refer to the concluding sentence of X, 3, before solving this problem.)

Problem 2.—(*a*) Show that for a perfect gas, equations (1*a*) and (1*b*) reduce to the form

$$C_p - C_v = R \tag{3a}$$

where R is the gas constant. (*b*) Show that for a gas which obeys Berthelot's equation of state (II, 10*b*), equation (1*a*) reduces to

$$C_p - C_v = R\left[1 + \frac{9}{128} \times \frac{24pT_c^3}{p_cT^3}\right] \tag{3b}$$

Problem 3.—By measuring the velocity of sound in a gas the value of the ratio, $\frac{c_p}{c_v}$, for that gas can be directly determined. In this way the specific heat ratio for xenon at 19° has been found to be $\frac{c_p}{c_v} = 1.666$. Calculate c_p, c_v, C_p and C_v for this gas.

2. Recent Theories of Energy Absorption.—The systematic investigations of specific heats at low temperatures carried out during the past 6 years largely by Nernst and his associates at

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[a] Frederick A. Lindemann. Investigator at the Institute for Physical Chemistry of the University of Berlin.

the University of Berlin have resulted in an extensive modification of former theories concerning heat capacity. Most of the recent attempts at a quantitative theoretical interpretation of these new results have been based upon a theory first advanced by Planck[b] and known as the "quantum" theory.[a] The development of this theory has given rise to several distinct kinds or varieties of "quantum" theory which are not entirely consistent with one another and none of which have as yet attained a very sharply defined character, although all of them contain the common element of assigning to radiant energy a discontinuous or atomic character of some kind. As applied by Nernst and others in the domain of specific heats the "quantum" theory is based upon the hypothesis that the molecules of a material substance do not absorb heat energy in a continuous manner but rather in discrete units or *quanta*.

In spite of the very considerable degree of fruitfulness which the quantum theory in its varied forms has had in several branches of physics, it is in many ways so indefinite, so difficult to conceive, and so unsatisfactory that it seems undesirable—and it is fortunately unnecessary—to attempt to employ it at the present time in interpreting for the beginner the known facts concerning heat capacity. We shall, therefore, base our presentation of the subject upon the older principle of the equipartition of energy, as modified by what may be termed the *constraint hypothesis*. This method of interpreting the known facts concerning heat capacity has recently received elaboration at the hands of Sir. J. J. Thomson,[5] G. N. Lewis[6] and others. It is a qualitative interpretation only and does not appear to be necessarily inconsistent with some kind of a "quantum theory," although its purpose is to render unnecessary the use of such a theory.

FLUIDS

3. Monatomic Gases.—When heat is absorbed at constant volume by a monatomic (I, 1c) perfect gas, the only effect which we should expect is an increase in the mean translatory kinetic energy of the molecules of the gas. There is apparently no other

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[a] Max Planck. Professor of Mathematical Physics and Director of the Institute for Theoretical Physics of the University of Berlin.

way in which the heat energy could be absorbed by such a gas, if we exclude the possibility of affecting the energy condition on the interior of the atoms or their rotational energy. On this hypothesis the molal heat capacity, C_v, of a monatomic gas can be easily calculated with the aid of the kinetic theory, in the following manner:

For one mole of *any* perfect gas the total translatory kinetic energy, E_k, possessed by its molecules, amounts according to equation (29, II) to

$$E_k=\frac{1}{2}\mathrm{N}mu^2=\frac{3}{2}RT \tag{4}$$

and if we add dQ calories of heat to the gas, thus causing its temperature to rise dT degrees, we would have for a *monatomic* gas at constant volume

$$\mathrm{d}Q=\mathrm{d}E_k=\frac{3}{2}R\mathrm{d}T \tag{5}$$

and hence, by definition,

$$C_v=\left(\frac{\partial Q}{\partial T}\right)_v=\frac{3}{2}R \tag{6}$$

or in words: C_v for a monatomic perfect gas is equal to $\frac{3}{2}R$ and is hence independent both of the nature of the gas and of its temperature and pressure. The experimental verification of this prediction was one of the earliest triumphs of the kinetic theory. Experiment has shown that for all monatomic gases $C_v=2.98$ cal. and in the case of helium, where the experiments have covered a wide temperature range, the value of C_v has been shown[7] to be the same at all temperatures within the range −256° to 2350°.

From equations (3a) and (6) it is also evident that for all monatomic perfect gases

$$C_p=\frac{5}{2}R=4.96\text{ cal.} \tag{7}$$

and

$$\gamma=\frac{c_p}{c_v}=1.666 \tag{8}$$

At extremely high temperatures it is of course conceivable that some of the electrons within the atoms of a monatomic gas might have their kinetic and potential energy (intra-atomic kinetic energy, Cf. X, 2) appreciably increased by the extremely short and violent impacts which take place between the atoms of the gas at these high temperatures. If such were the case, then evidently the value of C_v for a monatomic gas would become greater than $\frac{3}{2}R$. No temperature great enough to bring this about has as yet been attained in practice, however.

4. Diatomic and Polyatomic Gases.—Consider a perfect gas whose molecule is composed of n atoms. At a sufficiently low temperature these atoms will be held together so firmly by those forces which we call chemical affinity that the molecules will behave like perfectly rigid elastic bodies when they collide with one another. That is, the comparatively small force of the molecular impacts at very low temperatures will not be sufficient to produce an appreciable effect upon the positions of the atoms within the molecule, relative to one another. Moreover if the temperature is low enough, especially if as in the case of hydrogen the atoms have comparatively small masses, the moment of inertia of the molecule around its center of inertia will be so small that very little of the heat energy added to the gas would go toward increasing the rotational energy of its molecules.[6] In the neighborhood of the absolute zero, therefore, we might expect a polyatomic gas to behave like a monatomic one and we would thus have

$$C_v = \frac{3}{2}R \text{ (as } T \text{ approaches zero)} \tag{9}$$

As the temperature of the gas rises, however, the force of the impacts between the molecules gradually increases as the molecules move faster and faster. This force will eventually begin to affect the atoms within the molecule causing them to get farther apart with a consequent weakening of the forces holding the molecule together and an increase in the moment of inertia of the molecule. The energy of rotation of the molecule as a whole will therefore increase and the heat capacity of the gas will rise. At still higher temperatures the atoms within the molecule will begin to vibrate with wider and wider amplitudes, and thus more and more heat will be absorbed in molecular rotation and in intra-molecular vibration. Polyatomic gases are thus characterized by a constantly increasing heat capacity with rise in temperature. Eventually the temperature will become so great that the molecules will begin to be broken up into their constituent atoms, so powerful will be the force of the collisions, and an appreciable fraction of the molecules will be in this dissociated condition all of the time. In other words, we now have a chemical reaction to deal with and heat added to the gas will not only be absorbed in increasing molecular and intra-molecular motions but will also be in part absorbed by the chemical reaction which is taking place. The "apparent heat capacity" will therefore be a complex quantity, and to obtain what we shall call the "true heat capacity" of such a gas we shall have to subtract from the total heat required to raise the temperature of the gas 1° the amount of heat absorbed by the chemical reaction which accompanies this rise in temperature. As we go on increasing the temperature the "true" heat capacity evidently keeps on increasing owing to the fact that the number of molecules is increasing all the time due to the progressive dissociation of the gas. Eventually practically all the original molecules will be split up into their constituent atoms and C_v (true) will therefore approach the upper limit, $\frac{3}{2}nR$ cal.

To sum up then, for every polyatomic gas in the neighborhood of the absolute zero we should expect to have $C_v=\frac{3}{2}R$. As the temperature rises C_v will increase and will eventually approach the upper limit, C_v (true) $=\frac{3}{2}nR$, where n is the number of atoms in the molecule of the gas. This maximum temperature will be the higher the more stable the gas.

As an example of this behavior the values of C_v for hydrogen (H_2) may be cited. Between 35° and 60° absolute, Eucken[a] found[7] C_v for this gas to be constant and equal to 2.98 cal., that is, equal to $\frac{3}{2}R$, as in the case of monatomic gases. Hydrogen is the only gas which has been found to show this behavior at low temperatures. With other gases liquefaction intervenes and prevents the study of the gas in the neighborhood of the absolute zero. Above 60° absolute, C_v for hydrogen rises, at first fairly rapidly

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[a] Arnold Eucken. Privatdozent in Physical Chemistry at the University of Berlin.

and then more slowly, attaining the value 4.77 cal. at 0° C. From here on, the measured (*i.e.*, "apparent") values of C_v increase in accordance with the equation[8]

$$C_v = 4.51 + 0.0009T \tag{10}$$

up to the highest temperature (2000° C.) for which we have reliable measurements. In order to obtain the "true" value of C_v at high temperatures it is necessary, as explained above, to subtract from the "apparent" value the heat required for the chemical reaction $H_2 = 2H$. Specific heat measurements with hydrogen have not been carried to the very high temperature necessary to reach the limiting value C_v ("true") $= 2 \times \frac{3}{2}R = 3R = 5.96$; but in the case of iodine vapor (I_2) the dissociation into I atoms is known to be practically complete at 3000° and Bjerrum[a] has shown[9] experimentally that above this temperature the value of C_v is in fact equal to approximately 6 cal., as required by theory.

Problem 4.—According to Langmuir[b] [Jour. Amer. Chem. Soc., **37,** 441 (1915)], the heat of formation of hydrogen gas (H_2) out of atomic hydrogen at constant pressure is $H_P = 90{,}000$ cal. per mole at 3000° absolute; and at 2300° absolute the dissociation constant for this reaction is $\frac{p^2_H}{p_{H_2}} = K_p =$ 0.16 when pressure is expressed in millimeters of mercury. (*a*) Assuming that H_P varies with the temperature in accordance with the equation $H_P = H_0 - 2T$, where H_0 is an integration constant, calculate the degree of dissociation, α, of hydrogen at 1000°, at 2300°, and at 4000° absolute. (Cf. XIX, 5, and equations 45 and 55, XXII.) (*b*) Derive an expression for $\frac{d\alpha}{dT}$ (for $P = \text{const.}$) in terms of H_P, α and T. (*c*) Show that about 2.7 cal. of the "apparent" molal heat capacity of hydrogen at 2300° absolute is due to the displacement of the dissociation equilibrium. (*d*) Show that the "true" molal heat capacity of H_2 gas at 2300° absolute would be $C_v =$ about 4 cal. (*e*) At what temperature would the limiting value $C_v = 5.96$ cal. be attained (within 1 per cent.) in the case of hydrogen, (1) as to the "true" heat capacity of the gas, and (2) as to the "apparent" heat capacity of the gas? In all of the above calculations assume that $P = \text{const.} = 760$ mm.

[NOTE: The solution of this problem should not be undertaken until the study of Chapter XXII has been completed.]

[a] Niels Bjerrum. Since 1914, Professor of Chemistry at the School of Agriculture in Copenhagen.

[b] Irving Langmuir (1881–). Research Chemist for the General Electric Co., Schenectady, N. Y.

5. Liquids and Highly Compressed Gases.—Owing to the gradual transition from the gaseous state to the liquid state which is possible above the critical point (Cf. IV, problem 4), a liquid may be regarded as a limiting case of a gas which has been highly compressed and then cooled. Owing to the close proximity of the molecules in a liquid or a compressed gas and the consequent magnitude of the forces acting between the molecules, such a system is evidently a very complex one as regards its heat capacity. As we should expect, the heat capacity at constant volume will vary both with the temperature and with the nature of the liquid and owing to the complexity of the system no very important facts of general interest have as yet been discovered concerning the heat capacity of mobile liquids. Throughout the comparatively small temperature range within which mobile liquids are stable systems at ordinary pressures, the value of C_p appears to be a linear function of T for pure (*i.e.*, non-associated) liquids.

If, however, a liquid be supercooled until it assumes the glassy state (VII, 3), it loses all of its mobility and becomes a solid. Its heat capacity then decreases continuously with T and becomes zero when $T=0$, as is also the case with crystalline solids, and for the same reasons, as explained in the next section.

Associated liquids (XI, 2) dissociate gradually with rising temperature and hence part of their observed heat capacity is due to the heat required for the chemical reaction which is taking place. (Cf. Sec. 4.) The observed heat capacity may thus be very much larger than the "true" heat capacity. Thus the observed value of C_p for water at 0° is 18.141 cal. With rising temperature, it at first decreases until $t=27°$, after which it increases, increase being the normal behavior for a pure (non-associated) liquid. Owing to the large quantity of heat required for the depolymerization of the water with rising temperature the "apparent" specific heat capacity of water is the greatest of any known liquid.

CRYSTALLINE SOLIDS[10]

6. The Absorption of Heat by a Crystal. (*a*) **Very Low Temperatures.**—The molecules in the crystal network of a monatomic substance are held in definite positions by the action of the powerful crystal forces. As we have explained in a previous chapter (VII, 1), heat motion in a crystal at ordinary temperatures consists in an unordered oscillation of the molecules about their centers in the crystal network. In the neighborhood of the absolute zero the amplitudes of these oscillations will become vanishingly small and at the absolute zero the oscillations would probably cease entirely. Near the absolute zero, therefore, a crystal should behave like a perfectly elastic body even toward molecular impacts from the outside, that is, its constituent molecules would be so firmly bound together by the enormous crystal forces that the comparatively slight thermal impacts which at this low temperature the crystal could receive from the outside would not be powerful enough nor quick enough to set the individual atoms into a state of unordered oscillatory motion. Instead, the whole crystal would behave like one large molecule and the only way it could respond in any appreciable degree to molecular impacts from the outside would be by *vibrating* as a whole, in the way an elastic body does when it is struck. Heat energy absorbed by a crystal in the neighborhood of the absolute zero would therefore practically all be used up in setting the crystal into a state of *compressional* and *distortional vibration.*

With the aid of the theory of elasticity it should therefore be possible to deduce the relationship which connects heat capacity and temperature for solid substances in the neighborhood of the absolute zero. This has in fact been done[11] by Debye[a] and by Tolman by two different methods of reasoning both of which lead to the result that

$$c_v = \text{const.} \times T^3 \tag{12}$$

or

$$C_v = 71.9 \times \frac{T^3}{\theta^3} \tag{13}$$

In words, the heat capacity is proportional to the cube of the absolute temperature, the proportionality constant being characteristic of the substance. Equation (13), the form given by Debye, is simply equation (12) written for one mole of the substance and with its proportionality constant split for convenience into two parts, the part θ having the same dimensions as T and being a characteristic constant for each substance. The value of

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[a] Peter Debye (1884–). Since 1914, Professor of Physics at the University of Göttingen.

θ varies between such limits as $\theta = 50$ for calcium and $\theta = 88$ for lead up to $\theta = 1840$ for carbon in the form of the diamond.

As to the temperature range over which equation (13) holds, Debye states that it may be expected to give results correct to 1 per cent. up to $T = \frac{\theta}{12}$. Thus for cæsium it could be used only up to $T = \frac{50}{12} = 4°$ but for carbon it would hold up as high as $T = \frac{1840}{12} = 150°$. In Fig. 36 the graph of equation (13) is shown, taking C_v and T^3 as the variables and using for θ the values indicated. In the same figure the observed values of C_v for carbon and for aluminium are also given. The causes of the

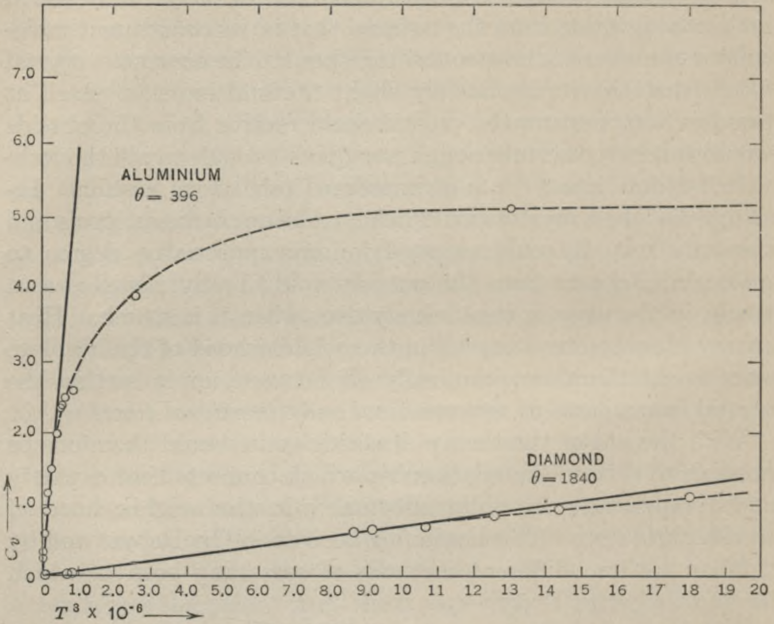

FIG. 36.—Illustrating the application of the Debye equation for the atomic heat capacity of solids at low temperatures. The circles represent observed values obtained in Nernst's laboratory. The dotted curves are drawn with reference to the observed values. The full lines are the graphs of Debye's equation (equation 13), using the values of θ indicated. [See further, Eucken and Schwers, Ber. Deutsch. Phys. Ges., **25**, 578 (1913).]

departure of the C_v values from equation (13) after a certain temperature is reached will now be considered.

(*b*) **Intermediate Temperatures.**—As we continue to heat the crystal, its molecules will at first slowly and then more rapidly begin to absorb some of the energy and to vibrate or oscillate as individuals in a random fashion about their centers in the crystal network. As soon as the amount of energy absorbed in this manner begins to become appreciable, equation (13) will evidently cease to hold, since it was derived on the assumption that no heat is absorbed in this manner. Moreover, the more powerful the crystal forces, and the smaller the mass of the molecules, the higher will the temperature have to be before the individual molecules can attain such oscillation frequencies that their kinetic energy of oscillation begins to be appreciable, for the kinetic energy of an oscillating body is proportional to its mass and to the square of its oscillation frequency. With a substance such as cæsium or lead which is soft and easily compressible and has a comparatively low melting point (Pb, 327° and Cs, 26°), the crystal forces must evidently be rather weak and hence its atoms can be set into random oscillation at a very low temperature and since furthermore they are very heavy atoms (see Table I), the energy which they can absorb in this way will be comparatively large. We see, therefore, why, in the case of a substance such as lead, we should expect deviations from equation (13) to appear very soon. In fact no measurements have been made with lead within the small temperature region ($T \ngtr 8^\circ$) where we could expect equation (13) to hold. The characteristic constant, θ, in that equation is evidently closely connected with the strength of the crystal forces and with the mass of the atoms of the crystal; in fact it varies directly with the former and inversely with the latter of these quantities.

On the other hand, in the case of a crystal such as the diamond, where we have extreme rigidity coupled with a very high melting point, the crystal forces must evidently be very powerful, and this fact coupled with the small mass of the atoms evidently requires that a fairly high temperature must be attained before the energy absorbed by the random oscillation of these atoms can begin to be appreciable. This accords with the fact that θ is very large and hence that equation (13) holds fairly well for this substance even up as high as $T = 220°$, as is evident from Fig. 36.

(*c*) **Moderate and High Temperatures. The Law of Dulong and Petit.**—If we continue to raise the temperature of our crystal, the energy absorbed by the oscillating molecules increases continuously and eventually the heat capacity will be determined almost entirely by the energy absorbed by these oscillating molecules and that which is absorbed in producing transverse and longitudinal vibrations through the crystal will soon become negligibly small. As the temperature increases and approaches the melting point of the crystal, the forces which are holding the molecules in their places in the crystal network will become so weak in comparison with the kinetic energy of these molecules, which now have large amplitudes of oscillation, that the crystal is almost ready to begin breaking up by melting. (Cf. VII, 1.) As this condition is approached the average kinetic energy of the oscillating molecules will therefore approach that of freely moving unrestrained molecules, such as those of a gas or liquid. This latter kinetic energy in the case of a monatomic substance is, as we have already seen (equation 4),

$$E_k = \frac{3}{2}RT \text{ cal. per mole} \qquad (14)$$

In addition to its kinetic energy a body oscillating about a center possesses potential energy (X, 1) also, that is, if the body were suddenly stopped in any part of its orbit, it would then fall into its center of attraction and on reaching this center would attain such a velocity that its kinetic energy would be the same as that which it possessed when moving in its orbit of oscillation. Potential energy and kinetic energy are therefore, on the average, equal in the case of a body oscillating about a center and hence for the total thermal energy, E_T, of $\mathbf{N}$ such oscillating molecules we would have

$$E_T = 2E_k = 3RT \qquad (15)$$

and hence by definition

$$C_v = \frac{\mathrm{d}E_T}{\mathrm{d}T} = 3R = 5.956 \text{ cal.} \qquad (16)$$

That is, with increasing temperature the atomic heat capacity (at constant volume) of every pure monatomic crystalline substance approaches the limit $3R$ or 5.956 cal.

In the case of most of the elements which are solids at ordinary temperatures (the exceptions are those of low atomic weight and high melting point such as carbon, boron, and glucinum), C_v has attained the average value 5.9 ± 0.1 cal. even at room temperatures.[12] Similarly for the same elements the values of C_p do not differ from 6.2 cal. by more than 0.2, *on the average*, so that even for specific heats at constant pressure and at room temperatures the product of specific heat and atomic weight is *approximately* a constant for nearly all the solid elements. This striking regularity was noticed in 1819 by Dulong[a] and Petit[b] and is known as Dulong and Petit's Law. It has been of considerable assistance in determining atomic weights in some instances.

Problem 5.—A certain element was found to combine with chlorine in the ratio of 1.376 parts to 1 part of chlorine and the specific heat capacity of the solid element was found to be $c_p = 0.032$ cal. per gram. Calculate an *exact* value for its atomic weight.

(*d*) **Very High Temperatures.**—We have seen (XVI, 2) that in metals there appear to be considerable numbers of electrons which are in a comparatively free condition, since they are able to pass from atom to atom within the crystal under the influence of an E.M.F. In the case of a metal with a fairly high melting point, such as platinum for example, we might therefore expect that at high temperatures the state of motion of the electrons would begin to be affected by the violently oscillating atoms and that considerable numbers of these electrons would consequently undergo an increase in their amplitude of oscillation, or their velocity of translation among the molecules, or both. If this should occur the value of C_v should then rise above the limit $C_v = 3R = 5.956$ cal.

Direct experimental confirmation of this conclusion is rather difficult to obtain owing to the fact that the necessary values of α and β in equation (1*b*) are not readily measured at high tem-

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[a] Pierre Louis Dulong (1785–1838). Professor of Physics at the Polytechnic School in Paris.

[b] Alexis Thérèse Petit (1791–1820). Professor of Physics at the Polytechnic School in Paris.

peratures. Corbino,[a] who has measured c_p for tungsten at 1500° estimates C_v to be as large as 7.8 cal. at this temperature[13] and Schubel[14] finds C_v for iron to be 7.5 cal. at 500°. High temperature data are, however, at present too fragmentary and uncertain to justify any general conclusions.

7. The Complete Heat Capacity Curve of a Crystal. (*a*) **General Features.**—We have discussed separately the three portions of the heat capacity curves for very low temperatures, for intermediate temperatures and for high temperatures, respectively. The characters of the complete C_v-T curve for a number of substances are shown in Fig. 37. For soft compressible substances with heavy atoms and low melting points (and consequently with small values of θ) the initial flat portion of the curve is very short and we have a very rapid rise to the final flat portion where C_v is nearly constant and equal to 5.9. Thus this value is reached in the case of lead (see Fig. 37) at as low a temperature as $t = -50°$.

As the mass of the atoms decreases and the melting point rises, θ increases and the character of the C_v-T curve changes as shown in the figure, the initial flat portion increasing in length, the subsequent rise becoming more gradual and the value $C_v = 5.9$ being attained only at higher and higher temperatures. Thus for silver C_v does not reach 5.9 cal. until $t = 240°$, and for aluminium t must be 760° before this value is attained. In the case of carbon it is not attained at any temperature within the range covered by the measurements and calculation indicates that the necessary temperature would lie above the melting point of this substance.

(*b*) **The Equations of Debye and of Nernst-Lindemann.**—For monatomic crystals, Debye[11] with the aid of a "quantum" theory (XX, 2) and other auxiliary hypotheses has derived a general quantitative relationship connecting C_v with T. This relationship contains only a single arbitrary constant, the constant θ already referred to. The curves drawn in Fig. 37 are the graphs of the Debye function employing the values of θ indicated. The points indicated by the centers of the circles are observed values of C_v for the three substances indicated. The close concordance between the positions of these points and the graphs of the Debye function indicates that the latter is capable of repre-

[a] Orso Mario Corbino. Professor of Physics at the University of Rome.

senting very closely the variation of C_v with T for these substances.

The complete equation of Debye is too complicated to reproduce here, but for all temperatures above $T = 0.34\theta$ (and with the exception of such elements as carbon, boron, and glucinum this means practically for all temperatures above $t = -150°$) it may be replaced without error greater than 1 per cent. by the following empirical equation of Nernst and Lindemann:[4]

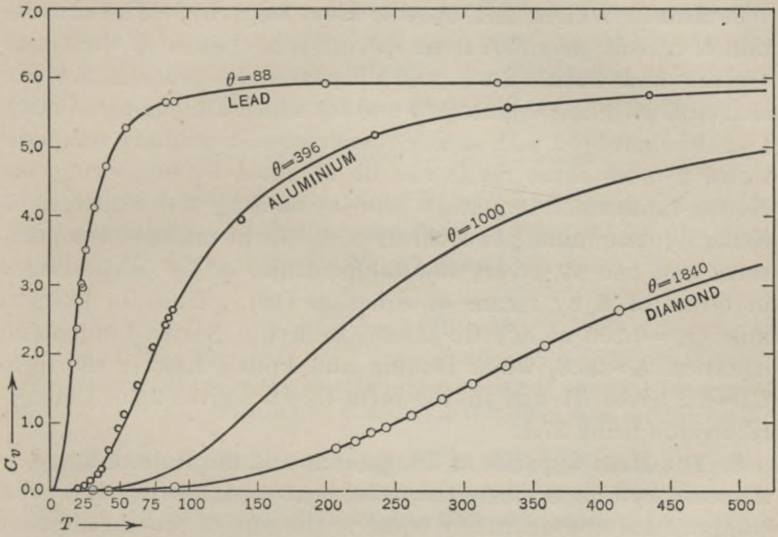

FIG. 37.—Illustrating the temperature variation of the atomic heat capacity of crystalline elementary substances. The circles represent observed values of C_v. The curves are graphs of Debye's complete equation, using the values of θ indicated, and are drawn without reference to the positions of the observed points.

$$C_v = \frac{3}{2}R\left[\frac{\left(\frac{\theta}{T}\right)^2 e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}} - 1\right)^2} + \frac{\left(\frac{\theta}{2T}\right)^2 e^{\frac{\theta}{2T}}}{\left(e^{\frac{\theta}{2T}} - 1\right)^2}\right] \tag{17}$$

in which e is the base of the natural logarithms. This equation evidently contains only one constant which depends upon the nature of the substance, namely, the constant θ whose significance we have already discussed, and even this constant can be calculated with sufficient exactness for many purposes from the atomic weight **A**, the density D, and the absolute melting point T_F of the substance by means of the following equation derived by Lindemann:[4]

$$\theta = 136\left(\frac{T_F}{\mathbf{A}}\right)^{\frac{1}{2}}\left(\frac{D}{\mathbf{A}}\right)^{\frac{1}{3}} \tag{18}$$

8. Atomic Weight and Specific Heat Capacity.—The calculation of atomic weight **A** from specific heat data with the aid of Dulong and Petit's Law was illustrated by problem 5. For elements with large values of θ and for which Dulong and Petit's Law does not hold with sufficient exactness at ordinary temperatures, a more exact result can be obtained by employing the Nernst-Lindemann equation and evaluating the constant θ either by determining two values of c_v, one at ordinary temperatures and one at a very low temperature, or by calculating θ in terms of **A** by means of equation (18). Thus for aluminium ($c_v = 0.200$ at 0°) we obtain from the Nernst-Lindemann equation $\mathbf{A} = 26.8$, while Dulong and Petit's Law in the form $C_p = 6.2$ gives 31 and in the form $C_v = 5.9$ gives 29.5, the correct value being 27.1.

9. The Heat Capacity of Compounds and the Rule of Kopp.—At ordinary temperatures the molal heat capacity (C_p) of a solid compound is approximately equal to the sum of the atomic heat capacities of its constituent elements. This statement is known as the rule of Kopp.[a] In employing Kopp's rule the value $C_p = 6.2$ should be employed as the average value for all the elements which at ordinary temperatures conform to Dulong and Petit's Law. For those which do not so conform and for those which in the free state are not solids at ordinary temperatures, individual values of C_p calculated from solid compounds containing the elements should be used. Thus suppose we wished to calculate the specific heat capacity of anhydrous $CuSO_4$. For Cu we could take $C_v = 6.2$. Sulphur does not conform to Dulong and Petit's Law, however, and oxygen is not a solid at ordinary temperatures. From a study of the heat capacities of various solid compounds containing these elements it has been found that in such com-

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[a] Hermann Kopp (1817–1892). Professor of Chemistry at the University of Heidelberg.

pounds these two elements appear to have on the average the following atomic heat capacities, for oxygen $C_p = 4$ cal. and for sulphur $C_p = 5.4$ cal. For the specific heat capacity of $CuSO_4$ we would therefore have

$$c_p = \frac{6.2 + 5.4 + 4 \times 4}{64 + 32 + 4 \times 16} = \frac{27.6}{160} = 0.17 \text{ cal.}$$

A still better procedure, however, would be to base the calculation upon an observed value (if such were available) of c_p for some analogous compound. Thus c_p for $ZnSO_4$ has been found to be 0.174 cal. and hence for one mole of $ZnSO_4$ we have

$$C_p = 0.174(66 + 32 + 4 \times 16) = 28.2 \text{ cal.}$$

and this must also be the value of C_p for $CuSO_4$ since Cu and Zn both obey the law of Dulong and Petit and hence have the same value for C_p. Hence for $CuSO_4$ we would have

$$c_p = \frac{28.2}{160} = 0.176 \text{ cal.}$$

Problem 6.—What is the specific heat capacity at constant pressure of Ag_2O, of CsBr, and of $RbBO_2$? Consult Landolt-Börnstein, 4th Ed. for the necessary data.

Problem 7.—The oxide of a certain metallic element contains 82.71 per cent. of the element and has a specific heat capacity at constant pressure of 0.0805 cal. What conclusion can be drawn respecting the atomic weight of the element?

HEAT CAPACITY AND REACTION HEAT

10. Constant Pressure Processes.—Consider any physico-chemical system in a state or condition which we will call A, the *initial condition.* Let the temperature and total pressure on the system be kept constant. Now suppose some isothermal process or processes (either chemical or physical, or both) to take place within the system, whereby it is transformed into a new condition which we will call B, the *final condition.* The reaction or process which takes place will be represented by A→B. The heat evolved by the system as a result of the reaction, A→B, we will call the heat effect, H_P, of the reaction. (Cf. XIX, 5.) The magnitude of the heat effect of a given isothermal reaction in a given system depends in general upon the temperature T at which the reaction in question takes place; and the quantitative relation between H_P and T can be readily derived with the aid of the First Law of Thermodynamics, as follows:

According to this law (see X, 4) the increase, ΔU, in the total energy, U, of the system, which accompanies any change in the condition of the system, is independent of the manner in which this change is brought about. For an isopiestic process the work, W, is also evidently independent of the nature of the process, because (see equation 3, X) $W = p\Delta v$, where Δv is the difference between the initial and the final volumes respectively of the system. It therefore follows from equation (1, X) that Q, the heat *absorbed* during the change, is also independent of the way in which the change occurs.

Suppose the system in question changes from the initial state A at the temperature T to the final state B at the temperature $T + \mathrm{d}T$. This change can occur in two ways:

(1) The reaction, A→B, may take place at the temperature T and the resulting system may then be heated from T to $T + \mathrm{d}T$. The total heat absorbed in this process would be

$$Q_1 = -H_P + C_{p_2}\mathrm{d}T \tag{19}$$

where H_P is the heat effect of the reaction at the temperature T and C_{p_2} is the total heat capacity of the system in the final state B.

(2) The system in the state A may first be heated from T to $T + \mathrm{d}T$ and the reaction, A→B, may then take place at the temperature $T + \mathrm{d}T$. The total heat absorbed in this process would be

$$Q_2 = C_{p_1}\mathrm{d}T - \left(H_P + \frac{\mathrm{d}H_P}{\mathrm{d}T}\mathrm{d}T\right) \tag{20}$$

where C_{p_1} is the heat capacity of the system in the initial state A.

But since Q is independent of the manner in which the change is brought about, we have $Q_1 = Q_2$, and therefore

$$-\frac{\mathrm{d}H_P}{\mathrm{d}T} = C_{p_2} - C_{p_1} = \Delta C_p \tag{21}$$

where ΔC_p is evidently the increase in heat capacity (at constant pressure) of the system which accompanies the reaction A→B.

Problem 8.—Integrate equation (21) on the assumption (1) that $\frac{d(\Delta C_p)}{dT}=0$ and (2) that $\frac{d^2(\Delta C_p)}{dT^2}=0$.

Problem 9.—Calculate ΔC_p for the chemical reaction $2\overline{H}_2+\overline{O}_2=2H_2O$, at room temperature, taking the necessary specific heat data from any suitable source. With the aid of equation (26, XIX) calculate H_P and also H_v $(=-\Delta U)$ for the above reaction at 100°.

Problem 10.—The specific heat capacity of ice is $c_p=0.50$ cal. per gram and its heat of fusion at 0° is 79.60 cal. per gram. (*a*) Show how equation (12, XIX) is obtained from these data. (*b*) The heat of sublimation of ice is almost independent of the temperature. Compute the specific heat capacity, c_p, of water vapor at 0°.

11. Constant Volume Processes.—For a constant volume process, the work performed against the external pressure is evidently zero (X, 5).

Problem 11.—Show by means of thermodynamic reasoning that for any process not involving electrical work

$$\frac{d(\Delta U)}{dT}=C_{v_2}-C_{v_1}=\Delta C_v \qquad (22)$$

where ΔC_v is the *increase* in the heat capacity of the system (at constant volume) which accompanies the change in its condition.

Problem 12.—Calculate $\frac{d(\Delta U)}{dT}+\frac{dH_P}{dT}$, for the reaction $\overline{CO}+\overline{O}=\overline{CO_2}$ at 2000°. (Cf. problem 10, XIX, and problem 11, above.)

THE INTERNAL ENERGY OF GASES

12. Perfect Gases.—Let us consider *one mole* of any perfect gas at the temperature T and pressure p_1 and endeavor to discover by thermodynamic reasoning the increase, ΔU, in the total or internal energy, U, of our gas, which occurs when the gas is allowed to expand isothermally from p_1 to some other pressure p_2. If it expands *reversibly*, that is, against an applied external pressure substantially equal at every moment to the pressure which it itself exerts, it will perform the maximum amount of work and this amount will be by definition (X, 9) the free energy, A, of the expansion process. From equation (2, X) we have $dW=pdv$ and hence

$$dW_{max}=pdv=\frac{RT}{v}dv=RTd\log_e v \qquad (23)$$

and

$$A=W_{max}=\int_{v_1}^{v_2}pdv=RT\log_e\frac{v_2}{v_1} \qquad (24)$$

from which by differentiating with respect to T we obtain

$$\frac{\mathrm{d}A}{\mathrm{d}T}=R\log_e\frac{v_2}{v_1} \tag{25}$$

Combining this with the Second Law equation (11, X), we find

$$Q=T\frac{\mathrm{d}A}{\mathrm{d}T}=RT\log_e\frac{v_2}{v_1} \tag{26}$$

whence

$$Q=A=W_{max} \tag{27}$$

and

$$\Delta U=Q-W_{max}=0 \tag{28}$$

or stated in words:

The internal energy of a perfect gas is independent of its pressure or volume. When the gas expands isothermally without doing work it neither absorbs nor evolves any heat, but if it does any work during its expansion, it then absorbs an amount of heat exactly equivalent to the work which it performs. This result was discovered empirically by Gay-Lussac and by Joule.[a] It is also one of the conclusions yielded by the kinetic theory of gases.

Problem 12.—With the aid of equation (22) demonstrate that *the heat capacity* (at constant volume), C_v, *of a perfect gas, is independent of its pressure or volume.* Is this also true for C_p?

13. Gases under High Pressures. The Liquefaction of Gases.[3]—When a gas under a high pressure is allowed to expand without doing work, some energy will be used up in separating the molecules against the attractive forces which exist between them (Cf. II, 10*a*), and if no heat is allowed to flow into the expanding gas, that is, if the expansion takes place *adiabatically*, the temperature of the gas will fall, provided its initial temperature is below a certain characteristic value known as the *inversion point* of the gas, the position of which varies with the pressure on the gas. This cooling effect (known as the "*Joule-Thomson*[b] *effect*"), which is zero in the case of perfect gases and very small for gases at moderate pressures, is frequently of considerable magnitude for gases under high pressures (see Table

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[a] James Prescott Joule (1818–1889). An English brewer.

[b] See footnote *a* p. 24.

XXVI) and it is employed technically for the liquefaction of gases in machines of the Linde and Hampson types.

TABLE XXVI

The Joule-Thomson effect for air, at the initial temperature t and the initial pressure P, when allowed to expand to a pressure of one atmosphere.

Δt = temperature fall in degrees.

Bradley and Hale, Phys. Rev., **29,** 258 (1909)

t	$P = 68$ Δt	$P = 102$ Δt	$P = 136$ Δt	$P = 170$ Δt	$P = 204$ atm. Δt
0°	17.1°	25.0°	32.6°	39.4°	44.6°
− 10	18.7	27.4	35.6	42.6	48.2
− 20	20.3	30.0	38.7	46.0	52.1
− 30	21.9	32.7	42.1	49.7	56.4
− 40	23.8	35.7	46.0	54.0	61.1
− 50	25.8	39.0	50.4	58.7	66.4
− 60	28.2	43.0	55.5	64.2	72.5
− 70	31.6	43.8	61.8	71.0	79.5
− 80	35.4	54.9	69.5	79.6	88.2
− 90	40.2	63.4	79.5	91.6	99.2
−100	47.4	74.3	92.8		
−110	57.2				

The cooling effect which accompanies the adiabatic expansion of a gas *which does work* during its expansion is much greater than the Joule-Thomson effect and, as we have seen in the preceding section, occurs even in the case of perfect gases. The technical application of this larger cooling effect to the liquefaction of gases was for a long time prevented by mechanical difficulties, but these were eventually overcome and the Claude liquid air machine makes use of this principle. The technical applications of these two principles in the Hampson, the Linde and the Claude machines are illustrated diagrammatically in Figs. 38 and 39, respectively.

In the Hampson and the Linde[a] machines the air, previously purified, compressed and cooled, enters the machine through the central tube T of a pair of concentric worms and on reaching the expansion valve M expands suddenly and is cooled as a result of the Joule-Thomson effect. The cold air then passes out through

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[a] Karl Paul Gottfried von Linde. Professor of Thermodynamics at the Institute of Technology in Münich.

the outer tube of the concentric worms to the compressor. But in passing out through this tube it obviously cools the entering air which, on subsequent expansion at the expansion valve,

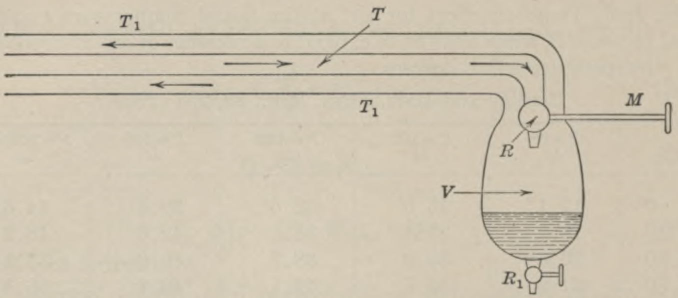

FIG. 38.—Diagrammatic representation of the Linde liquid air machine.

attains a lower temperature until finally this progressive cooling results in the liquefaction of part of the air, which then collects in V and is drawn off through the valve R.

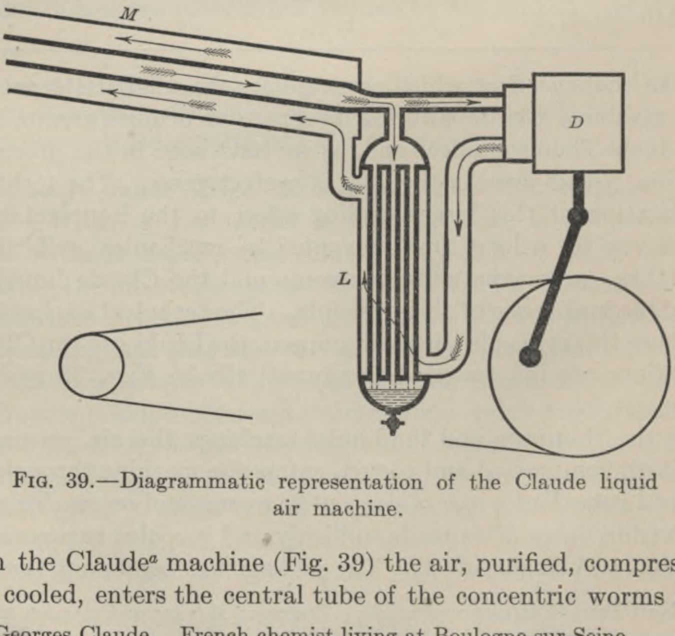

FIG. 39.—Diagrammatic representation of the Claude liquid air machine.

In the Claude[a] machine (Fig. 39) the air, purified, compressed and cooled, enters the central tube of the concentric worms and

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[a] Georges Claude. French chemist living at Boulogne-sur-Seine.

passes into the expansion chamber, D, of an air-engine, either a turbine or a piston machine similar to a steam engine. Here it expands and does work in driving the engine and as a result undergoes a correspondingly large fall in temperature, about 95 per cent. of the heat loss representing the energy supplied to the engine and the remaining 5 per cent. being due to the Joule-Thomson effect. The cold air then passes up and around a set of tubes L similar to a boiler and connected with the feed supply as indicated. The air in these tubes is cooled by the expanded air which then passes out through the outer tube of the concentric worms and serves to cool the entering air. This process goes on until finally the air in the tubes L begins to liquefy and collects in the bottom of the compartment, whence it is drawn off at regular intervals by an automatic valve. The engine driven by the expanding air is connected to an air compressor and assists in compressing the air which is to be fed into the machine.

14. The Pressure-Volume Law for the Adiabatic Expansion of a Perfect Gas.—For any process involving only *infinitesimal* energy changes, the equation of the First Law of Thermodynamics may be written

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W = \mathrm{d}Q - p\mathrm{d}v \tag{29}$$

whence,

$$\mathrm{d}U = \left(\frac{\partial Q}{\partial T}\right)_v \mathrm{d}T = \text{(by definition) } mc_v\mathrm{d}T \tag{30}$$

For an adiabatic process

$$\mathrm{d}Q = 0 \text{ (by definition)} \tag{31}$$

and hence for such a process equation (29) becomes

$$mc_v\mathrm{d}T + p\mathrm{d}v = 0 \tag{32}$$

For a perfect gas

$$mT = \frac{M}{R}pv \tag{33}$$

and (see equation 3a)

$$R = M(c_p - c_v) \tag{34}$$

Combining these equations with equation (32) so as to eliminate T, we find

$$\mathrm{d}\log_e p + \frac{c_p}{c_v}\mathrm{d}\log_e v = 0 \tag{35}$$

which on integration gives

$$pv^{\frac{c_p}{c_v}} = pv^{\gamma} = \text{const.} \tag{36}$$

This equation shows the manner in which p and v vary during the adiabatic expansion of a perfect gas. The specific heat ratio, $\gamma = \frac{c_p}{c_v}$, is of course a constant for a given gas.

Problem 14.—Give all the steps in the derivation of equation (36) from equation (32).

Problem 15.—With the aid of equation (36) derive the relation connecting p and T during the adiabatic expansion of a perfect gas.

Problem 16.—Four moles of a perfect monatomic gas at 0° and a pressure of 0.1 atmosphere are allowed to expand reversibly until the pressure falls to 0.1 mm. Calculate in liter atmospheres the work done: (1) if the expansion takes place isothermally, and (2) if it takes place adiabatically.

Problem 17.—When air at 0° is allowed to expand suddenly from an initial pressure of five atmospheres to a final pressure of one atmosphere it is cooled 1.1° by the Joule-Thomson effect. If it performed maximum work during this adiabatic expansion, *approximately* how much would it be cooled? The specific heat ratio for air is 1.40. (Cf. problem 15.)

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CHAPTER XXI

CHEMICAL KINETICS

HOMOGENEOUS SYSTEMS

1. Rate of Reaction.—The rate at which a chemical reaction proceeds in a homogeneous (I, 8) system is defined as the decrease in the equivalent concentration of the reacting molecular species in the time, dt, divided by that time, or mathematically

$$\textit{rate of reaction} = -\frac{\mathrm{d}C}{\mathrm{d}t} \tag{1}$$

Experiment shows that in gaseous systems and in dilute solutions in which the thermodynamic environment is kept constant the rate of any chemical reaction is proportional to the product of the concentrations of the reacting molecular species, each concentration being raised to a power equal to the number of molecules of the corresponding molecular species which enter into the reaction, as shown by the chemical equation which expresses the reaction *as it actually takes place.* Thus if the reaction whose rate is being measured is expressed by the equation

$$a\mathrm{A}+b\mathrm{B}+\ .\ .\ .\ .\ \rightleftarrows m\mathrm{M}+n\mathrm{N}+\ .\ .\ . \tag{2}$$

then the law just stated would be expressed by the equation

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t}=-\frac{\mathrm{d[B]}}{\mathrm{d}t}=k[\mathrm{A}]^a[\mathrm{B}]^b\ldots \tag{3}$$

where the brackets, [A], [B], etc., signify the concentrations, *at the time*, t, of the molecular species, A, B, etc., expressed in *equivalents per liter*. This law is known as Guldberg[a] and Waage's[b] law of chemical mass action as applied to reaction rate. The constant, k, is known as the **specific reaction rate.**

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[a] Cato Maximilian Guldberg (1836–1902). Professor of Applied Mathematics in the University of Kristiania.

[b] Peter Waage (1833–1900). Professor of Chemistry at the University of Kristiania.

If the above reaction does not go to *completion* in the direction indicated by the arrow, the rate of the reverse reaction must also be considered. This would evidently be

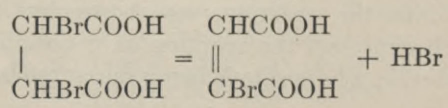
$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{N}]}{\mathrm{d}t} = k'\,[\mathrm{M}]^m[\mathrm{N}]^n\ldots \qquad (4)$$

and the *resultant* rate *in the direction indicated by the arrow* would be the difference between the actual rates of the two opposing reactions, that is,

$$-\frac{\mathrm{d}_r[\mathrm{A}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} + \frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k[\mathrm{A}]^a[\mathrm{B}]^b\ldots - k'[\mathrm{M}]^m[\mathrm{N}]^n\ldots \qquad (5)$$

In what follows we shall confine the consideration to the rates of reactions which run practically to completion in one direction, that is, reactions in which k' is negligibly small.

2. First Order Reactions.—Reactions in which the concentration of only one reacting substance *changes* are called first order reactions, provided only one molecule of this reacting substance appears in the chemical equation which expresses the reaction as it actually takes place. The change of dibrom-succinic acid into brom-maleic acid, which occurs when it is boiled with water, is an example of a reaction of this type.



$$\begin{array}{l}\mathrm{CHBrCOOH}\\ |\\ \mathrm{CHBrCOOH}\end{array} = \begin{array}{l}\mathrm{CHCOOH}\\ \|\\ \mathrm{CBrCOOH}\end{array} + \mathrm{HBr}$$

Another example is the hydrolysis of cane sugar in dilute aqueous solution in the presence of an acid. The reaction is

$$\mathrm{C_{12}H_{22}O_{11}} + \mathrm{H_2O} = \underset{\text{glucose}}{\mathrm{C_6H_{12}O_6}} + \underset{\text{fructose}}{\mathrm{C_6H_{12}O_6}}$$

Problem 1.—*Two* reacting substances, water and sugar, evidently are involved in this reaction. How can it be a first order reaction according to the above definition?

For a first order reaction the general law of reaction rate, equation (3), evidently reduces to the form

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}] \qquad (6)$$

or if we call A the *equivalent concentration* of the reacting substance when the measurements of the reaction rate are begun (*i.e.*, when $t=0$), and x the number of equivalents (per liter) which have disappeared as a result of the reaction, at the end of t units of time, then *at the time* t we have $[\mathrm{A}]=A-x$ and $-\mathrm{d}[\mathrm{A}]=\mathrm{d}x$, and equation (6) may be written in the form

$$\frac{\mathrm{d}x}{\mathrm{d}t}=k(A-x) \tag{7}$$

Problem 2.—Show that the integral of this equation is

$$\frac{1}{t}\log_{10}\frac{A}{A-x}=0.4343\ k \tag{8}$$

Problem 3.—In a solution at 48° containing 0.3 mole of cane sugar in a liter of 0.1 normal HCl, it is found (by means of a polarimeter) that 32 per cent. of the sugar is hydrolyzed in 20 minutes. (*a*) Calculate the proportionality constant, k, which is known as the specific reaction rate. (*b*) Calculate the rates of the reaction at its start and at the end of 30 minutes. (*c*) What per cent. of the sugar will be hydrolyzed at the end of 60 minutes? (*d*) What per cent. of the sugar would be hydrolyzed at the end of 30 minutes if the 0.3 mole had been initially dissolved in 10 liters of the $0.1n$ HCl instead of in 1 liter? The HCl acts merely as a catalyst (XX, 12). It is not used up during the reaction.

3. Second Order Reactions.—When *two* reacting molecular species or two molecules of the same species simultaneously disappear as a result of the reaction, under conditions such that the concentrations of *both* decrease, then the reaction is classed as a second order reaction.

Examples:

(1) The saponification of an ester by an alkali,

$$CH_3COOCH_3+NaOH=CH_3COONa+CH_3OH$$

(2) The polymerization of NO_2 in the gaseous state,

$$2NO_2=N_2O_4$$

Problem 4.—If A is the initial concentration of one of the reacting substances and B that of the other, and x is the number of equivalents, per liter, of each which have been changed over by the reaction after t units of time, show that the equation for the rate of the reaction may be written,

$$\frac{\mathrm{d}x}{\mathrm{d}t}=k(A-x)(B-x) \tag{9}$$

The general integral of this equation is

$$\frac{1}{(A-B)t}\log_{10}\frac{B(A-x)}{A(B-x)}=0.4343k \tag{10}$$

Problem 5.—If A and B are equal or if the two reacting molecules are of the same kind show that the integral is

$$\frac{1}{t}\,\frac{x}{(A-x)A}=k \tag{11}$$

Problem 6.—In the saponification of methyl acetate (CH_3COOCH_3) by caustic soda, 20 per cent. of the ester will be saponified in 10 minutes when the initial concentrations are both 0.01 molal. (*a*) How long will it take to saponify 99 per cent.? (*b*) What will be the concentration of methyl alcohol at the end of half an hour? If the initial concentration of the ester is 0.015 mole and that of the NaOH 0.03 mole per liter, (*c*) what per cent. of the ester will be saponified in 10 minutes, (*d*) how long will it take to saponify 99 per cent., and (*e*) what will be the concentration of methyl alcohol at the end of half an hour?

4. Third Order Reactions.—This order includes all reactions in which *three* reacting molecules are directly involved with concentration decrease.

Example:

$$2CH_3COOAg+HCOONa=2Ag+CO_2+CH_3COOH+CH_3COONa$$

The three molecules here are two molecules of silver acetate and one of sodium formate. The equation for the rate of this reaction would evidently be

$$\frac{dx}{dt}=k(A-x)^2(B-x) \tag{12}$$

5. Reactions of Higher Orders.—Reactions of higher orders than the third are of very rare occurrence. For example, the reaction which is written

$$2PH_3+4O_2=P_2O_5+3H_2O$$

represents the combustion of the gas PH_3. This would apparently be a reaction of the *sixth order* since six reacting molecules are involved. Experiment shows, however, that the rate of this reaction actually corresponds to the equation of a second order reaction. The interpretation placed upon this fact is that the above reaction actually occurs in stages. The first stage is the slow reaction, $PH_3+O_2=HPO_2+H_2$. This is evidently a second order reaction. The subsequent reactions by which H_2O and P_2O_5 are produced are very rapid in comparison with the first stage so that the rate which is actually measured experimentally is the rate of the first stage of the reaction, which accounts for the fact that the reaction behaves as a second order one. The rate of a reaction which occurs in stages can obviously never be greater than the rate of the slowest stage and this is the reason why reactions of higher orders are so rarely met with. The slowest stage of the reaction determines its order and the slow stages are practically always either first, second or third order reactions.

6. Saponification and the Ionic Theory.—

Problem 7.—(*a*) In dilute solution the rate of saponification of ethyl acetate by $Ba(OH)_2$, $Ca(OH)_2$, or $Sr(OH)_2$ is found to obey the equation of a *second order reaction* and to have a specific reaction rate only slightly smaller than in the case of saponification with NaOH. Stoichiometrically the reaction would be written

$$2CH_3COOC_2H_5 + Ba(OH)_2 = (CH_3COO)_2Ba + 2C_2H_5OH$$

and would appear to be a third order reaction. Show how according to the Ionic Theory we should expect the reaction to be a second order one and to have nearly the same specific reaction rate as in the case of NaOH. (*b*) The specific reaction rates for saponification with KOH, LiOH and CsOH are the same as for NaOH, but that for NH_4OH is very much smaller (initially only about $\frac{1}{50}$ as large, in fact, for a 0.1 normal solution). All the reactions are second order ones. How are these facts interpreted by the Ionic Theory? (Suggestion: Write all the reactions in the ionic form and make use of the facts stated in XVII, 3. Esters are non-electrolytes.)

Problem 8.—At 25° the initial rate of saponification of ethyl acetate by 0.01 normal NaOH is 9.0 times as great as that by 0.1 normal KCN. From the conclusions reached in problem 7, together with the data given in XVII, 3 and Table XXIII, what would you conclude as to the concentration of hydroxyl ion in the KCN solution? The source of this hydroxyl ion will be explained later (equation 25, XXIII).

7. Reaction Rate and Thermodynamic Environment. The Neutral Salt Effect.—Reaction rates in solution are usually appreciably influenced by the presence of neutral salts which apparently have nothing directly to do with the reaction itself. In many cases this "neutral salt effect," as it is called, may be interpreted as due, at least partially, to the influence of the ions of the salt upon the thermodynamic environment (XVII, 6) prevailing within the solution, for the rate of any given reaction is very powerfully influenced by the nature of the medium in which it takes place. In employing reaction rates for determining the concentration of some molecular species in a given solution it is, therefore, essential that the experiments be conducted as far as possible under comparable conditions as regards thermodynamic environment. Thus in problem 8, the NaOH solution employed in the experiment *should have been* one which had an OH^--ion concentration as close as possible to that prevailing in the KCN solution, and it should also have contained sufficient KCl to make its total concentration of uni-univalent electrolyte 0.1 equivalent per liter. The thermodynamic environment within the NaOH solution would then probably have been as close to that prevailing within the KCN solution as it is possible to make it. Only when the thermodynamic environments are identical in two solutions are we justified in assuming that a given reaction has the same specific reaction rate in both solutions. This should be borne constantly in mind in employing the laws of chemical kinetics in the study of solutions.

8. Temperature and Reaction Rate.—It has been found in many cases that equal increments of temperature produce about the same multiplication of reaction rate. For each rise of 10° the rate of the reaction is multiplied 2–4 fold, the exact value of the multiplying factor varying with the nature of the reaction.

Problem 9.—Assuming 2.5 as an average value for this multiplying factor calculate how many fold the reaction rate would be increased by a rise of 100°.

A more general expression for the effect of temperature upon the specific reaction rate is that formulated by van't Hoff as follows:

$$\frac{\mathrm{d}\log k}{\mathrm{d}T} = \frac{A}{T^2} \tag{13}$$

where A is a characteristic constant.

CATALYSIS

9. The Phenomenon of Catalysis.—The rate of chemical reactions in many instances can be greatly increased by the presence in the reaction mixture of substances, called **catalytic agents** or **catalysts,** which are not themselves consumed by the reaction. This phenomenon is known as **catalysis.** There are many kinds and varieties of catalysts and the mechanism of their action is so different in different cases and so little understood that few, if any, general principles can be laid down concerning the phenomenon. It is of immense importance, however, in scientific and industrial processes as well as in many processes which occur in nature, and a brief statement regarding what is known concerning the action of some classes of catalysts will be included here.

10. Contact Agents.—Many reactions both in the gaseous state and in solution are greatly accelerated near the surface of certain solids such as platinum black, ferric oxide and other metallic oxides. Such substances in a finely divided state **adsorb** (that is, concentrate upon their surface) the reacting substances from the gas or solution and the reaction in the adsorbed layer then proceeds much more rapidly than in the body of the gas or solution where the concentrations are much lower. This is supposed to be the mechanism of the catalytic effect of some of the contact agents. The action appears in many cases, however, to be a very specific one. The contact process of sulphuric acid manufacture is an example of a technical application of a contact agent.

11. Carriers.—In many cases the catalyst actually reacts chemically with one of the reacting substances to form an intermediate compound which in turn reacts in such a way as to regenerate the catalyst and produce the final reaction products. Such catalysts are known as **carriers.** Thus nitric oxide, NO, acts as a carrier in the familiar chamber process for the manufacture of sulphuric acid.

$$O_2+2NO=2NO_2$$

and then

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

12. Ions as Catalysts.—Hydrogen ion and hydroxyl ion act as catalysts for many reactions which occur in aqueous solution. The velocity of any reaction catalyzed by either of these two ions is, in dilute solution, directly proportional to the concentration of the ions in question as long as the thermodynamic environment remains constant. The inversion of cane sugar by an acid, the hydrolysis of an ester by an acid and the hydration of milk sugar by an alkali are examples of such reactions. They are frequently employed for the purpose of determining the concentration of the catalyzing ion in a given solution.

13. Enzymes.—Many animal and vegetable organisms secrete certain complex colloidal compounds, known as enzymes, which possess highly specific but very powerful catalytic powers. Thus the yeast plant secretes the enzyme, invertase, which is able to convert cane sugar into glucose and fructose, while another yeast enzyme known as xymase will convert glucose (but not the closely related compound, fructose) into alcohol and carbon dioxide. On the other hand, glucose will be converted into lactic acid by an enzyme produced by the lactic acid bacillus. Enzymes are responsible for many of the processes of physiology (as pepsin, lypase, and trypsin in digestion) and for the processes of decay of dead animal and vegetable matter. The velocity of reactions catalyzed by enzymes increases with the temperature up to a point usually between 30° and 40° after which it decreases owing to the destruction of the enzyme by heat. Enzymes are employed in a number of industrial processes such as brewing and butter and cheese manufacture.

14. Water as a Catalyst.—The presence of water seems to be indispensable for the occurrence of many reactions. Thus HCl and NH_3 when brought together in a perfectly dry condition will not react with each other. The presence of the merest trace of water vapor, however, suffices to start the reaction. The mechanism of this action is not understood but it seems to resemble in some respects the effect of a percussion cap in setting off an explosive. Once started the reaction is able to proceed of itself without further assistance.

15. Autocatalysis.—Some reactions are catalyzed by the presence of one or more of their own reaction products and are, therefore, said to be autocatalyzed. The reaction between oxalic acid and a permanganate in solution is catalyzed in this manner. The decomposition of Ag_2O into Ag and O_2 at high temperatures is catalyzed by the metallic silver and the rate of the reaction increases with the amount of silver. The action in this instance, however, is probably a contact action, the reaction $2O = O_2$ being catalyzed at the surface of the finely divided silver.

16. Radiant Energy.—Many reactions which proceed very slowly or inappreciably in the dark are greatly accelerated when illuminated by radiant energy of the proper wave length. The union of H_2 and Cl_2 gases and the changes which take place upon a photographic plate are examples of **photochemical reactions.** Not only is the reaction rate influenced by the light, but the nature of the reaction products and the yield obtained are also affected. The subject of photochemistry is being extensively investigated at the present time. Other forms of energy such as the silent electric discharge, X-rays, cathode rays, etc., also exert a powerful influence upon the course and rate of chemical reactions in many cases. These effects, while introduced at this point, are not usually classed as catalytic, however.

HETEROGENEOUS SYSTEMS

17. Solid Substances.—When a solid substance reacts with a substance in solution the rate of the reaction is proportional to the surface of the solid exposed to the solution. When a solid dissolves in its own solution the rate at which it dissolves, $\frac{dC}{dt}$, under uniform conditions of temperature and of stirring is proportional to the surface, A, exposed and to the difference between its solubility, S (XIV, 12), and its concentration, C, in the solution at the time t, or mathematically

$$\frac{dC}{dt} = kA(S-C) \tag{14}$$

Problem 10.—(*a*) What are the relative rates at which a substance will dissolve in its own solution (1) when the solution is 50 per cent. saturated and (2) when it is 98 per cent. saturated? (*b*) If it takes 2 minutes for the solution to become 50 per cent. saturated, how long should a solubility experiment last, if one wishes to determine the solubility with an accuracy of 0.01 per cent.? Assume constant surface and constant conditions of stirring.

CHAPTER XXII

CHEMICAL EQUILIBRIUM

A. Homogeneous Systems at Constant Temperature

1. The Nature of Chemical Equilibrium.—Suppose that we bring together in any homogeneous gas or liquid system two substances A and B which enter into chemical reaction with each other to form the substances M and N as expressed by the equation

$$aA + bB = mM + nN \tag{1}$$

As this reaction proceeds, the concentrations of A and B will be observed to decrease and those of M and N to increase, at first rapidly and then more slowly until finally a steady condition will be reached in which the concentrations of the molecular species A, B, M and N no longer change, that is, the reaction has apparently stopped. In the same way if we were to start with the two substances M and N at the same initial equivalent concentrations as were used for A and B in the first experiment, we would find that reaction (1) would proceed *from right to left* until eventually a steady condition of no concentration change would again be reached. The concentrations of the four molecular species when this steady state is attained are found to be independent of the direction from which this condition is approached. That is, whether we started with a moles of A and b moles of B or with m moles of M and n moles of N, the concentrations of all four species when the reaction had apparently ceased would have the same respective values regardless of the direction in which the reaction took place. When a steady condition of this character is reached in any chemical reaction, the molecular species involved are said to be in **chemical equilibrium** with one another. This equilibrium is not a static one, however, but is instead a dynamic one. That is, the chemical reaction does not actually cease but rather it continues to take place in both directions but at the same rate in each direction.

The reacting substances are thus re-formed by the reverse reaction just as fast as they are used up by the direct reaction, the net concentration change being zero.

The concentrations of the reacting molecular species when equilibrium is attained will be called their **equilibrium concentrations.** In any chemical equilibrium in a perfect gas or a dilute solution at a given temperature, the equilibrium concentrations, C_{A}, C_{B}, C_{M} and C_{N}, are always so related that they fulfill the following condition

$$\frac{C_{\mathrm{M}}^{m}\cdot C_{\mathrm{N}}^{n}}{C_{\mathrm{A}}^{a}\cdot C_{\mathrm{B}}^{b}}=\text{const.} \tag{2}$$

where the value of the "*equilibrium constant,*" as it is called, is, for a given thermodynamic environment, characteristic of the reaction in question. This relation is Guldberg and Waage's law of chemical mass action as applied to chemical equilibrium. In section 3 we shall recognize it as a special case of a more general law based upon the principles of thermodynamics.

2. The Criterion for True Chemical Equilibrium.—The fact that in any instance a given chemical reaction has apparently come to a stop cannot be taken as proof that a *true* chemical equilibrium has been attained. In order to make certain the equilibrium should be approached from both directions. If the value of the equilibrium constant computed from the equilibrium concentrations is found to be independent of the direction from which the equilibrium is approached, then the equilibrium is a true chemical equilibrium. False equilibria are sometimes met with, due to various causes such as destruction or absence of an essential catalytic agent (XXI, 9), extreme slowness of some stage of the reaction, or slow diffusion of one or more of the substances involved. False equilibria occur most frequently in the case of reactions in heterogeneous systems.

Problem 1.—In one experiment 0.100 mole each of H_2 and CO_2 are heated together at 686° in a closed liter vessel until the reaction has apparently ceased. The vessel is then found to contain 0.0422 mole of H_2O. In a second experiment 0.110 mole of CO and 0.0902 mole of H_2O are heated in the same way and when the reaction has apparently ceased 0.0574 mole of CO_2 is found to have been formed. Was true chemical equilibrium attained in these experiments?

3. The Thermodynamic Law of Chemical Equilibrium at Constant Temperature. (*a*) **Gaseous Systems.**—If any number of molecular species A, B, ..., M, N, . . etc., are in chemical equilibrium with one another in the gaseous state as expressed by the equation

$$a\mathrm{A}+b\mathrm{B}+\ .\ .\ \rightleftharpoons m\mathrm{M}+n\mathrm{N}+\ .\ .\ .\ .\ . \qquad (3)$$

the following purely thermodynamic (XII, 8) relationship can be shown to connect the partial pressures, p, and molal volumes, v, of the molecular species concerned, at any given constant temperature T (see Appendix, 12, for derivation):

$$mv_{\mathrm{M}}\mathrm{d}p_{\mathrm{M}}+nv_{\mathrm{N}}\mathrm{d}p_{\mathrm{N}}+\ .\ .\ .\ -av_{\mathrm{A}}\mathrm{d}p_{\mathrm{A}}-bv_{\mathrm{B}}\mathrm{d}p_{\mathrm{B}}-\ .\ .\ .\ =0 \quad (4)$$

where dp for each substance represents the complete differential $\mathrm{d}p=\left(\frac{\partial p}{\partial P}\right)_x\mathrm{d}P+\left(\frac{\partial p}{\partial x}\right)_P\mathrm{d}x$, P being the total pressure on the system and x the mole fraction of *any constituent* of the system whether it be concerned in the chemical reaction or not. In other words, if the chemical equilibrium be displaced in one direction or the other by changing either the pressure or the composition of the gas or both, the corresponding changes in the partial pressures of the molecular species concerned in the equilibrium must occur in such a way as to fulfill the condition represented by equation (4), which for brevity may be written

$$\Sigma^{\pm}mv_{\mathrm{M}}\mathrm{d}p_{\mathrm{M}}=0 \qquad (5)$$

where the ± sign indicates that the terms for the substances on one side of the reaction must be taken with opposite signs from those for the substances on the other side of the reaction.

In order to integrate this equation it is first necessary to know the equation of state for each molecular species involved. If all the substances obey the perfect gas law or in general if p represents the fugacity (XIV, 1), we have $mv_{\mathrm{M}}\mathrm{d}p_{\mathrm{M}}=mRT\mathrm{d}\log_e p_{\mathrm{M}}$ $=RT\mathrm{d}\log_e p_{\mathrm{M}}^m$ and similarly for each of the other substances involved in the reaction. Equation (5) therefore becomes

$$RT\mathrm{d}\log_e\frac{p_{\mathrm{M}}^m\cdot p_{\mathrm{N}}^n\ .\ .}{p_{\mathrm{A}}^a\cdot p_{\mathrm{B}}^b\ .\ .}=0 \qquad (6)$$

which on integration gives

$$\frac{p_{\mathrm{M}}^m\cdot p_{\mathrm{N}}^n\ .\ .}{p_{\mathrm{A}}^a\cdot p_{\mathrm{B}}^b\ .\ .}=\mathrm{const.}=K_p \qquad (7)$$

This is the law of chemical mass action (for a gaseous system) expressed in terms of partial pressures or fugacities. If the substances are all perfect gases, we may also write $p_{\mathrm{M}}^m = (C_{\mathrm{M}}RT)^m$ and similarly for each of the other substances, where $C\left(=\frac{1}{v}\right)$ represents the equilibrium concentration in moles per liter (XXII, 1) in each instance. Equation (7) may therefore be written

$$\frac{C_{\mathrm{M}}^m \cdot C_{\mathrm{N}}^n \cdot\ \cdot}{C_{\mathrm{A}}^a \cdot C_{\mathrm{B}}^b \cdot\ \cdot} = K_p(RT)^{\Delta n} = K_c \tag{8}$$

where

$$\Delta n = a + b + \ .\ .\ . - m - n - \ .\ .\ . \tag{9}$$

and we thus obtain the mass action law (equation 2) in terms of volume concentrations. The relationship between the equilibrium constants, K_p and K_c, of the two modes of expression is shown in equation (8) from which one constant can evidently be calculated if the other is known.

Problem 2.—Show that for perfect gases the mass action law may also be written in terms of the mole fractions of the substances concerned, thus

$$\frac{x_{\mathrm{M}}^m \cdot x_{\mathrm{N}}^n\ .\ \ .}{x_{\mathrm{A}}^a \cdot x_{\mathrm{B}}^b\ .\ \ .} = K_p P^{\Delta n} = K_x \text{ (if } P \text{ is constant)} \tag{10}$$

(*b*) **Liquid Systems.**—In the case of a chemical equilibrium in solution, equation (7), where p represents fugacity, must evidently hold for the vapor above the solution and if the thermodynamic environment in the solution is constant, the fugacity of each molecular species will be proportional to its mole fraction, x, in the solution. (See equation 1, XIV.) Equation (7) may, therefore, be written

$$\frac{x_{\mathrm{M}}^m \cdot x_{\mathrm{N}}^n}{x_{\mathrm{A}}^a \cdot x_{\mathrm{B}}^b} = \text{const.} = K_x \tag{11}$$

for the solution. This is the law governing a chemical equilibrium in any solution in which the thermodynamic environment is constant.

Problem 3.—Show that from the nature of the definitions (XI, 5) of x and C for any substance in a solution the following relationship exists

$$\frac{C_{\mathrm{M}}^m \cdot C_{\mathrm{N}}^n}{C_{\mathrm{A}}^a \cdot C_{\mathrm{B}}^b} = K_x(C_0 + C_{\mathrm{A}} + C_{\mathrm{B}} + \ldots + C_{\mathrm{M}} + C_{\mathrm{N}} + \ldots)^{-\Delta n} \tag{12}$$

where Δn and K_x are defined by equations (9) and (11) respectively and C_0 represents the total concentration (in moles per liter) of all molecular species in the solution which are not directly concerned in the reaction (solvent molecules, for example).

Problem 4.—Under what mathematical condition and also under what other practical condition will equation (12) reduce to the form

$$\frac{C_{\mathrm{M}}^{m} \cdot C_{\mathrm{N}}^{n} \cdot \ \cdot}{C_{\mathrm{A}}^{a} \cdot C_{\mathrm{B}}^{b} \cdot \ \cdot} = \text{const.} = K_c \tag{13}$$

In writing the mass action law in terms of concentrations it is frequently customary to employ the formula of the substance inclosed in brackets as a symbol representing its volume concentration. Thus in this nomenclature equations (2) and (13) would be written

$$\frac{[\mathrm{M}]^m}{[\mathrm{A}]^a} \frac{[\mathrm{N}]^n}{[\mathrm{B}]^b} \cdot \ \cdot \ \cdot = K_c \tag{14}$$

4. Determination of the Equilibrium Constant.—In order to determine by direct measurement the numerical value of the equilibrium constant for a given reaction at a given temperature, it is first necessary to *establish equilibrium* between the different substances taking part in the reaction and then to measure the concentration of each substance in this equilibrium mixture. In order to be certain that true equilibrium has been attained, it should, as explained above, be approached from both directions and in many cases a catalyst (XX, 9) must be used in order to hasten the attainment of equilibrium. The method employed for determining the concentration of any substance in an equilibrium mixture must be one which does not change this concentration during the process of determining its value, for such a change would result in a displacement of the equilibrium. The customary methods of chemical analysis cannot, therefore, be employed in many cases and we are obliged to modify these methods or to resort to physical methods for measuring the equilibrium concentrations of the molecular species concerned.

As an example we will consider the problem of determining the equilibrium constant for the gaseous reaction

$$2\mathrm{HI} \rightleftarrows \mathrm{H}_2 + \mathrm{I}_2 \tag{15}$$

Equilibrium in this reaction may be reached either by heating gaseous HI to the desired temperature or by heating a mixture of H_2 and I_2 gases to the same temperature. This equilibrium is attained very slowly at ordinary temperatures but at the temperature of 440° it is reached in a short time. If, therefore, we heat a known quantity of HI (or of H_2 and I_2) at 440° in an equilibrium vessel of known volume until equilibrium is reached, we may determine the equilibrium concentrations by drawing out a sample of the mixture through a cooled capillary tube connected with the equilibrium vessel and then analyzing this sample at our leisure, for the mixture on being drawn into the capillary is cooled so quickly that the rate of reaction is reduced nearly to zero before any appreciable shifting of the equilibrium can occur and the composition of the cold sample will be the same as that of the equilibrium mixture at the higher temperature. In one experiment[1] of this kind Bodenstein[a] heated 20.55 moles of H_2 with 31.89 moles of I_2 to 440° until equilibrium was attained. The equilibrium mixture was then rapidly cooled and on analysis (by absorbing the I_2 and HI in caustic potash and measuring the H_2 remaining) was found to contain 2.06 moles of H_2, 13.4 moles of I_2 and 37.0 moles of HI in the volume, v. Hence

$$\frac{[H_2][I_2]}{[HI]^2} = \frac{\left[\frac{2.06}{v}\right]\left[\frac{13.4}{v}\right]}{\left[\frac{37}{v}\right]^2} = K_c = 0.020$$

Instead of cooling such an equilibrium mixture and then analyzing it, it is frequently possible to determine its composition at equilibrium by a suitable physical method. Thus in the present case HI and H_2 are both colorless gases while I_2 is strongly colored, and by comparing the depth of color of the equilibrium mixture with that of a series of vessels containing iodine vapor alone, at known concentrations, the composition of the equilibrium mixture can be determined.

Problem 5.—A 1-liter glass tube containing 0.1 mole of HI gas is heated to 440° until equilibrium is established. By comparing the depth of the violet color observed on looking through the tube with the color of standard tubes containing pure iodine vapor, the color of the equilibrium mixture is found to correspond to an I_2 concentration of 0.0112 mole per

[a] Max Bodenstein (1871–). Professor of Physical and Electrochemistry in the Technical School at Hannover, Germany.

liter. From these data compute the equilibrium constant for this equilibrium. (Cf. XI, problem 1.)

Problem 6.—A liter vessel containing 0.14 mole of H_2 and 20.6 grams of iodine is heated to 440°. How much HI will be formed? What will be the partial pressure of each substance when equilibrium is reached? What will be the total pressure of the mixture?

Problem 7.—x grams of HI are heated in a 2-liter vessel at 440° until equilibrium is reached, the total pressure being 0.5 atmosphere. Calculate x.

When a gas containing more than one atom in its molecule is heated to a sufficiently high temperature it breaks up or dissociates partly into simpler molecules (XX, 4) and the fractional extent to which such dissociation occurs at any given temperature and pressure is called the **degree of dissociation**, α, of the gas. This degree of dissociation and hence also the equilibrium constant of the reaction can usually be calculated by determining the density of the partially dissociated gas in equilibrium with its dissociation products at the temperature in question and comparing this observed density, $D_{\text{obs.}}$, with the density, $D_{\text{calc.}}$, which the gas would have at the same temperature, if it did not dissociate. This latter density can of course be calculated from the molecular weight of the undissociated gas and the temperature and pressure.

Problem 8.—When one molecule of a gas dissociates it produces n molecules of dissociation products. If one mole of the gas is heated to such a temperature that the degree of dissociation is α, show that the total number of moles of all molecular species present in the dissociation mixture is $1+(n-1)\alpha$. Show also that α can be calculated from the equation

$$\alpha=\frac{D_{\text{calc.}}-D_{\text{obs.}}}{(n-1)D_{\text{obs.}}} \tag{16}$$

Problem 9.—N_2O_4 dissociates in the gaseous state according to the equation

$$N_2O_4=2NO_2 \tag{16a}$$

At 49.7° and 26.8 mm. the observed density of the gas referred to air is 1.663. Calculate its degree of dissociation.

Problem 10.—Show that for any dissociation of the type, $AB=A+B$, the equilibrium constant, K_c, for the dissociation reaction is expressed by the relation

$$\frac{\alpha^2C}{1-\alpha}=K_c \tag{17}$$

and for the type, $A_2 = 2A$, by the relation

$$\frac{\alpha^2 C}{1-\alpha} = \frac{K_c}{4} \tag{18}$$

where C is the volume concentration of the dissociating substance calculated on the assumption that it does not dissociate, that is, $C = \frac{m}{M} \div v$, where m is the number of grams of the substance in the volume v.

Problem 11.—From the data in the preceding problems calculate the value of K_c for the dissociation of N_2O_4 at 49.7°. Calculate also K_p and K_x for one atmosphere pressure. From your results calculate α for $P = 1$, for $P = 0.5$, and for $P = 0.1$ atmosphere respectively. What would be the partial pressure of the NO_2 molecules for $P = 0.6$ atmosphere. Calculate the actual density (referred to air) of the gas, for $P = 93.75$ mm. (The observed value at this pressure is 1.79.)

Problem 12.—Phosphorous pentachloride dissociates in the gaseous state according to the equation

$$PCl_5 = PCl_3 + Cl_2$$

When 1 gram of PCl_5 crystals is vaporized at 182° and 1 atmosphere the density of the vapor referred to air is 5.08 when equilibrium is reached. Calculate α, K_c, K_p and K_x. Calculate the degree of dissociation of the PCl_5 after equilibrium is reached in each of the following experiments: (*a*) 10 grams of Cl_2 are mixed with the PCl_5, (1) at constant volume and (2) at constant pressure; (*b*) the same experiments with 1 gram of Ar; (*c*) the same experiments with 1 gram of PCl_3; (*d*) the total pressure is reduced to 0.5 atmosphere; (*e*) the volume is increased to 50 liters by reduction of pressure.

Problem 13.—At 290° and 330° respectively the sublimation pressures (VI, 1) for NH_4Cl crystals are 185.3 and 610.6 mm. respectively. The measured values for the density of the saturated vapor at the same two temperatures are 0.00017 and 0.00053 gram per cubic centimeter respectively. Calculate the degree of dissociation and the equilibrium constant for each temperature.

Problem 14.—Preuner and Brockmöller[2] found that 0.0755 gram of selenium vapor occupying a volume of 114.2 c.c. at 700° exerts a pressure of 185 mm. The selenium is in a state of dissociation equilibrium in accordance with the reaction $Se_6 \rightleftharpoons 3Se_2$. Calculate α, K_p and K_c. What pressure would be exerted by 0.0369 gram of selenium vapor in a volume of 148 c.c. at 700°? [Value observed = 86.5 mm.]

5. Chemical Equilibrium in Solutions of Constant Thermodynamic Environment.

—All chemical equilibria in solutions where the thermodynamic environment remains constant must obey the law of mass action as expressed by equations (11) and (13), since for such solutions this law is a purely thermodynamic deduction. The application of the mass action law to such solutions is so similar to the corresponding applications of equation (8) to gaseous equilibria that no special discussion will be required.

6. Ionization Equilibria in Solution. (*a*) **General.**—We have already seen (XVII, 6) that in solutions containing ions the thermodynamic environment is a function of the ion concentration and cannot, therefore, be treated as a constant, if the ion concentration changes. For an equilibrium involving ions we are thus not in a position to connect equation (7) with the mole fractions (in the solution) of the molecular species involved in the equilibrium, except by the use of purely empirical relationships (such as equations (16, 17 and 18, XVII)) connecting fugacity with ion concentration. While a dilution law can be derived in this way (Cf. problem 15), it will usually not be the most convenient one and in the following pages, therefore, the laws governing ionization equilibria will be presented mainly as purely empirical relations.

(*b*) **The General Dilution Law for Uni-univalent Electrolytes.**—The ionization of a uni-univalent electrolyte, CA, is expressed by the equation (XV, 3)

$$\mathrm{CA} \rightleftharpoons \mathrm{C}^+ + \mathrm{A}^-$$

and the equilibrium expression for dilute solutions is

$$\frac{[\mathrm{C}^+][\mathrm{A}^-]}{[\mathrm{CA}]} \quad \text{(see equation 13)}$$

If the solution contains no other electrolytes, then from the definition of α it follows (see problem 10) that

$$\frac{[\mathrm{C}^+][\mathrm{A}^-]}{[\mathrm{CA}]} = \frac{\alpha^2 C}{1-\alpha} \tag{19}$$

where C is the *total concentration* of the electrolyte in moles per liter.

If we assume that the ratio, $\frac{\Lambda\eta}{\Lambda_0\eta_0}$, is a measure of the degree of ionization of a uni-univalent electrolyte as expressed by equation (12, XVII), then the two empirical equations of Kraus and Bates (XVII, 1*c*) connecting conductance and concentration assume the forms

$$\frac{\alpha^2 C}{1-\alpha} = k + k'(\alpha C)^h \tag{20}$$

and

$$\log \frac{\alpha^2 C}{1-\alpha} = k + k'(\alpha C)^h \tag{21}$$

respectively. We have already seen (XVII, 1*c* and Table XXII) that these empirical dilution laws are capable of accurately representing conductance data for a great variety of electrolytes both in aqueous and in non-aqueous solutions.

In general the sum of the concentrations of all the species of positive ions (or of negative ions) in any solution is called the **total-ion concentration** of that solution. In the case now under consideration (a solution of a uni-univalent electrolyte) there is evidently only one species of positive ion, C-ion, present in significant amount in the solution and hence the total-ion concentration of our solution is αC, the expression which occurs on the right-hand side of equations (20) and (21). The facts represented by the two empirical equations (20) and (21) may, therefore, be summed up in the following words: If we accept the conductance ratio, $\Lambda\eta/\Lambda_0\eta_0$, as a measure of the degree of ionization of a uni-univalent electrolyte, then the equilibrium expression for the ionization reaction of such an electrolyte is in general not a constant, at constant temperature, but increases as the total-ion concentration of the solution increases.

(*c*) **Strong Electrolytes.**—When, however, we come to classify the uni-univalent electrolytes with reference to their behavior in this connection, we find that for practical purposes they may be roughly divided into two groups. In the first group fall the strong electrolytes (XV, 4 and XVII, 3). For these electrolytes the term $k'(\alpha C)^h$ in equations (20) and (21) is always either of the same order of magnitude or much larger than the term k. In other words, the total-ion concentration is always a controlling factor in the ionization of this group of electrolytes, the tendency to ionize, as measured by the magnitude of the equilibrium expression, being greater the greater the ion concentration of the solution.

The fact that the ionization equilibrium of strong electrolytes, even in very dilute solutions, is so greatly at variance with the law of mass action is due chiefly to the behavior of the un-ionized molecules of these electrolytes. The deduction of that law assumes that the molal fugacity of every molecular species concerned in the equilibrium is constant under all conditions. While this condition is approximately fulfilled by the ions, the un-ionized molecules deviate from it very widely as we have already seen (XVII, 6). The effect of this deviation (the causes of which we have already discussed) upon the character of the law governing the ionization equilibrium will be more clearly appreciated by solving the following problems.

Problem 15.—With the aid of equations (16 and 17, XVII) derive a dilution law for KCl.

Problem 16.—Calculate the value of the equilibrium expression for the ionization of KCl (*a*) at 0.0001*n*, (*b*) at 0.01*n*, and (*c*) at 0.25*n*. See Table XXII.

(*d*) **Weak Electrolytes.**—In the second group fall the weak electrolytes. For these electrolytes the term $k'(\alpha C)^h$ is always small in comparison with the term k and evidently becomes smaller the more dilute the solution. For most purposes, therefore, the term $k'(\alpha C)^h$ may be neglected in comparison with the term k in the case of weak electrolytes in dilute solution and equations (20) and (21) on this assumption both reduce to the form

$$\frac{\alpha^2 C}{1-\alpha} = \text{const.} = K_c \qquad (22)$$

an equation which we have already met under the name of Ostwald's dilution law (XVII, 1*c*).

In other words the ionization of weak electrolytes in dilute solution takes place in accordance with the law of mass action. (See equation 19.) The weaker the electrolyte, that is, the smaller the numerical value of its **ionization constant,** K_c, the more closely is the mass action law obeyed. Even if the ion concentration of the solution be greatly increased by adding a strong electrolyte to it, the resulting change in the thermodynamic environment will cause (see XVII, 6) only comparatively small changes in the fugacities of the ions and un-ionized molecules of the weak electrolyte, and hence the ionization constant of such an electrolyte may for most purposes be assumed to have approximately the same value in all dilute solutions in a given solvent and at a given temperature, regardless of what other substances may be present, at small concentration, in the solution. In concentrated solutions and for solutions containing large additions of other substances, particularly electrolytes, this statement no longer holds true, however. The behavior of a typical weak electrolyte is illustrated in the following problem and table.

TABLE XXVII

Conductance and Viscosity Data for Acetic Acid Solutions at 25°. Based upon Measurements by Kendall[4] and by Rivett and Sidgwick.[5] For Illustrating the Behavior of a Typical Weak Electrolyte with Respect to the Law of Mass Action.

V K	C R. & S.	$D\ 25°/25°$ R. & S.	$\overline{L}\times10^4$	Λ	η/η_0 R. & S.	α	$K_c\times 10^5$	$K_x\times 10^7$
6948.0	....	1.0000	0.1682	.....	1.0000		1.87	3.36
3474.0	....	1.0000	0.2496	.....	1.0000		1.87	3.37
1737.0	....	1.0000	0.3661	.....	1.0000		1.85	3.34
868.4	....	1.0000	0.5312	.....	1.0001		1.85	3.32
434.2	....	1.0000	0.7651	.....	1.0002		1.86	3.34
217.1	....	1.0000	1.097	.....	1.0005		1.85	3.34
108.6	....	1.0000	1.564	.....	1.001		1.85	3.33
54.28	....	1.0001	2.227	.....	1.002		1.86	3.34
27.14	....	1.0003	3.165	.....	1.004		1.87	3.36
13.57	....	1.0007	4.485	.....	1.008		1.88	3.39
7.908	....	1.0011	....	4.618	1.014		1.86	3.38
3.954	....	1.0022	....	3.221	1.028		1.86	3.38
1.977	....	1.0043	....	2.211	1.056		1.85	3.38
	(0.7443)	1.0065	(13.21)	.....	1.082		1.83	3.38
0.989	....	1.0084	....	1.443	1.112		1.74	3.27
	1.489	1.0122	16.71	.....	1.169		1.70	3.22
	2.006	1.0162	17.89	.....	1.230		1.62	3.12
	2.977	1.0235	18.54	.....	1.347		1.40	2.80

Problem 17.—In Table XXVII are given the values of the conductances of a series of aqueous solutions of acetic acid at 25°. Under V is given the "*dilution*" of the solution, that is, the volume (in liters) containing one equivalent of the acetic acid. Calculate in each instance the molal concentration, C, of the solution and the degree of ionization, α, and tabulate your results in the corresponding columns. The value of Λ_0 for acetic acid at 25° can be obtained from the data in Table XXI. For the higher concentrations where the viscosity of the solution is appreciably different from that of water, its influence may be approximately taken account of by using equation (12, XVII) to calculate α. For this purpose the relative

viscosity, η/η_0, of each solution is given in the table. Finally, as explained in section (3*b*) and problem 4, the equilibrium constant for a reaction in solution should in general be expressed in mole fractions instead of volume concentrations. That is, the quantity K_c would not necessarily be constant except in the more dilute solutions. In general the quantity K_x should be employed. The value of K_x for any solution is most conveniently calculated from the corresponding value of K_c with the aid of equation (12). For this calculation the density of the solution will be required and density data are therefore included in Table XXVII. Note that the calculation of K_x in this way involves the assumption that the molecular weight of water in the liquid state is 18. After calculating the values of K_c and K_x for all of the solutions, construct graphs with values of C as ordinates and corresponding values of K_c and K_x respectively as abscissæ.

Up to how high a concentration can the viscosity influence in the case of acetic acid be neglected, if an accuracy of 1 per cent. is desired in the value of α? Up to what concentration can (*a*) volume concentrations and (*b*) mole fractions be safely employed in formulating the equilibrium expression, without producing an appreciable deviation from constancy? The answers to these questions are largely governed by the accuracy of the experimental data and the student may form an estimate of this from his construction of the above graphs.

A satisfactory interpretation of the decrease in the value of K_x for acetic acid above $0.25n$ is rendered very difficult by the uncertainty which exists with regard to the validity, at the higher concentrations, of several of the factors and assumptions involved in the calculation. An analysis of the nature and effects of these factors is valuable as an example of the difficulties (already briefly discussed, XIV, *d*) of drawing any reliable conclusions concerning the individual behaviors and effects of several variables by the study of a derived relationship involving them all. A consideration of these factors will also serve to exemplify some of the difficulties which are encountered when we attempt to extend our solution laws into concentrated aqueous solutions of electrolytes, difficulties which some chemists,[6] impatient at the slow progress which physical chemistry is making in this important field, seem unable to appreciate.

The factors and assumptions involved in attempting to determine and analyze the behavior of acetic acid with respect to the mass action law in the more concentrated solutions are as follows:

(1) A constant value for K_x is only to be expected if the thermodynamic environment remains constant. Owing to the slight degree of ionization of the acetic acid the influence of the ions

upon the thermodynamic environment could scarcely be appreciable within the range covered by Table XXVII, however, and their influence may therefore be neglected in comparison with the effects of the other factors. The direction of their influence would be to produce an increase in the value of K_x with increasing ion concentration.

(2) The thermodynamic environment changes with increasing concentration of the acetic acid molecules. The direction and magnitude of this effect is not known, but judging from the corresponding influence of the alcohols (Fig. 25), it is probably not important for concentrations below $0.5n$.

(3) In the above calculations the conductances of the ions are assumed to be inversely proportional to the viscosity of the solution. The viscosity correction at $0.25n$ amounts to nearly 6 per cent. in the value of the equilibrium constant and the effect of applying the correction is to increase the computed value of this constant.

Ninety per cent. of the conductance of acetic acid is due to hydrogen-ion, and our knowledge of the variation of the conductance of this ion with the viscosity of the medium is not yet sufficiently complete to enable us to determine the magnitude of the error introduced in assuming that it obeys Stokes' Law. If hydrogen-ion behaves like the other uni-univalent ions (and a partially completed investigation in the author's laboratory shows that this is approximately the case) (Cf. equation 13, XVII), then the values of K_x computed in Table XXVII would be somewhat *overcorrected* for the viscosity influence, thus causing them to be larger than they should be.

(4) In computing the mole fractions of the solute molecules, the molecular weight of the water is taken as 18. This is of course not correct (II, 5), but the effect of this assumption would not influence the constancy of the computed values of K_x if the average molecular weight of the water itself remained constant. It does not do so, however, but probably decreases as the concentration of the acetic acid increases, owing to the shifting of the association equilibrium which takes place in accordance with Le Chatelier's Theorem (Sec. 11 below). The effect of such a decrease is to cause the *computed* values of K_x to increase

slowly with increasing concentration of the acetic acid. The magnitude of this effect cannot at present be determined.

(5) The ionization of the acetic acid does not take place as represented by the simple equation

$$HAc = H^+ + Ac^-$$

but involves the solvent also, as explained previously (XV, 3). A more nearly correct method of writing the ionization reaction would be

$$HAc + (H_2O)_a = [H(H_2O)_b]^+ + [Ac(H_2O)_c]^-$$

and the mass law expression could then be written

$$\frac{x_{H^+} \cdot x_{Ac^-}}{x_{HAc}} = p^a_{H_2O} \cdot \text{const.} \qquad (23)$$

where x represents mole fraction and p fugacity or vapor pressure. In sufficiently dilute solutions the vapor pressure of the water may be assumed to be practically constant, but it decreases with increasing concentration of the solute. The effect of neglecting to take account of the change in the vapor pressure of the water with increasing concentration is to cause the calculated values of the equilibrium constant for the higher concentrations to come out too small. This is the behavior shown by the values of K_x computed in Table XXVII.

The value of a in equation (23) is not known, and even if it were, the uncertainties in the other factors involved in the problem would make it impossible to make any trustworthy calculation for the concentrated solutions. A much better degree of constancy in the calculated value of K_x can of course be obtained by treating a as an empirical constant to be evaluated from the experimental data, but no particular significance is to be attached to the value of a thus obtained or to the better constancy which would result, since a two-constant equation can always be made to fit a given set of values more accurately than one containing only a single arbitrary constant.

(6) The amount of water combined with the molecules and ions of the solute should be subtracted from the total quantity of water present in the solution before computing the values of the mole fractions. (Cf. equation 23, XIV.) Neglecting to do this would not have any appreciable effect at the lower concentra-

tions, but with increasing concentration of the solute it would cause the computed values of K_x to be too small. The concentration at which this effect would begin to be appreciable in the case of acetic acid is not at present known but it could be approximately determined by suitable experiments.

(7) In the above calculations the acetic acid is assumed to be entirely non-associated in the solution. With increasing concentration we know, however, that it becomes more and more associated because pure acetic acid is a highly associated liquid. To what extent the influence of this factor is appreciable in the concentration range covered by Table XXVII is difficult to determine. The effect of association would be to cause the computed values of K_x to be too large.

Owing to the conflicting effects of the factors just discussed it is evidently impossible to determine the concentration range within which the ionization equilibrium of acetic acid actually obeys the mass action law with a given degree of accuracy; nor would an answer to this question be, *per se*, of very much value, since it would not give us the desired information concerning the questions involved in the separate factors discussed above. The answers to such questions are not to be obtained from the constancy or lack of constancy displayed by the computed values of an equilibrium constant, but must be sought for by means of more direct evidence, involving as few variables as possible. For the purpose of calculating values of Λ it is important to note the empirical fact that K_c is substantially constant up to $C = 0.5$, but no theoretical significance is to be attached to this fact or to the fact that K_x is constant over a trifle wider range than K_c. A one-constant *empirical* equation which holds over a still wider concentration range has recently been proposed by Kendall.[4]

(*e*) **Ionization in Mixtures of Electrolytes.**—In mixtures containing weak electrolytes it will, as just stated, be sufficiently exact for most purposes to assume that all such electrolytes obey the law of mass action. If the mixture contains only one strong electrolyte, the degree of ionization of this electrolyte may be assumed to be practically uninfluenced by the presence of any weak electrolytes, but if more than one strong electrolyte be present, the ionization equilibrium of each strong electrolyte will be influenced by the presence of the ions of the other strong electrolytes and the general problem of calculating the degree of ionization of the strong electrolytes in such a mixture is a complex one. It is usually solved by estimating the total ion concentration, C_i, of the mixture by a series of approximations and then assuming that the expression

$$\frac{[\mathrm{C}^+][\mathrm{A}^-]}{[\mathrm{CA}]}=k+k'(C_i)^h \tag{24}$$

or

$$\log\frac{[\mathrm{C}^+][\mathrm{A}^-]}{[\mathrm{CA}]}=k+k'(C_i)^h \tag{25}$$

or some other empirical relationship holds for each electrolyte in the mixture, with the same values for the empirical constants as are obtained from the ionization of that same electrolyte in its own pure solutions at the same temperature.

This assumption, namely, that the equilibrium expression for a strong electrolyte in a mixture is the same function of the total-ion concentration as it is in a pure solution of that electrolyte, was first made by Arrhenius and is usually known as the **isohydric principle.** The chief evidence in favor of the validity of this principle rests upon the fact that the measured specific conductance of a mixture of two electrolytes agrees fairly well with the specific conductance calculated from this principle. This agreement is likewise almost if not quite as good if the isohydric principle be formulated in the following approximately identical and more convenient form: *The equilibrium expression for a strong electrolyte in a mixture in which the total concentration of all strong electrolytes is C equivalents per liter is the same as it is in a pure solution of that electrolyte at the same equivalent concentration.* The roughly approximate rule that all uni-univalent strong electrolytes are ionized to the same extent at the same concentration has already been stated (XVII, 3). In so far as this rule is valid, it is evident that, if a solution contains several uni-univalent strong electrolytes, the equilibrium expressions for all of these electrolytes in that solution must be equal to each other.

Problem 18.—On the basis of the isohydric principle demonstrate the truth of the following rule: *If two uni-univalent strong electrolytes having one ion in common (e.g.,* KCl *and* NaCl) *are in solution together, the degree of ionization of each electrolyte in the solution is equal to the value which that* *electrolyte has in its own pure solution at such a concentration, C, that αC in that solution is equal to C_i in the mixture.*

The rule given in problem 18 may also be formulated in the following approximately identical and more convenient form: *If two uni-univalent strong electrolytes having one ion in common (e.g.,* KCl *and* NaCl) *are in solution together, the degree of ionization of each electrolyte in the solution is equal to the value which that electrolyte has in its own pure solution at a concentration equal to the sum of the concentrations of the two electrolytes in the mixture.*

Very recently Kraus has suggested[3] another principle for calculating degrees of ionization in mixtures. This principle is based upon the assumption that the ionization of a strong electrolyte is determined by the product of the concentrations of its own ions in the solution instead of by the total-ion concentration of the solution. On this basis the degree of ionization of a strong electrolyte in any mixture, where its *ion-product* is I, is the same as its degree of ionization in its own pure solution at such a concentration that its ion-product is also I. The conductance data for mixtures seem to agree somewhat better with the assumption made by Kraus, but the difference in the results obtained by the two methods of calculation is not very large in the cases where they have been compared. The question as to which of these two methods of calculating degrees of ionization in mixtures is more nearly correct must be left for future investigation. In many cases they will give practically the same results.

PROBLEMS

Note.—In all problems dealing with ionization equilibria in solution at 18° or 25°, the necessary Λ_0 values are to be computed from Table XXI. Other conductance data required, if not to be found in this book, may be taken from the Landolt-Börnstein tables or from any other reliable source. A critical summary of conductance data for aqueous solutions of strong electrolytes has been prepared by A. A. Noyes and K. G. Falk [Jour. Amer. Chem Soc., **34,** 461 to 472 (1912)] and a very complete compilation of similar data for many weak electrolytes can be found in Scudder's *Conductivity and Ionization Constants of Organic Compounds.*

Problem 19.—If 0.1 mole of HCl is added to a liter of 0.1 normal acetic acid at 18°, what will be the acetate-ion concentration in the resulting solution?

Problem 20.—How much sodium acetate must be added to 1 liter of a 0.2 molal acetic acid solution at 18° in order to decrease the hydrogen-ion concentration 100-fold?

Problem 21.—On the basis of the isohydric principle in its simpler form, calculate the concentration of each species of ion in the following mixtures at 18°: 1 liter of a solution contains (*a*) 0.1 mole each of KCl and NaCl; (*b*) 0.1 mole each of $NaNO_3$ and NaCl; (*c*) 0.005 mole of $AgNO_3$ and 0.1 mole of KNO_3; (*d*) 0.1 mole each of KNO_3 and NaCl; (*e*) 0.005 mole of TlCl and 0.1 mole of KNO_3.

Problem 22.—At 25° and 0.02*n*, cumic acid is 4.88 per cent. ionized while glycolic acid is 8.3 per cent. ionized. If a liter of one solution is mixed with a liter of the other, what will be the concentration of hydrogen-ion in the resulting solution?

Problem 23.—The same as 22 with acetic acid in place of cumic acid.

Problem 24.—The same as 22 with hydrochloric acid in place of cumic acid.

Problem 25.—In what proportions should 0.01 normal cumic acid and 0.01 normal glycolic acid be mixed in order to obtain a solution (*a*) with the minimum hydrogen-ion concentration; (*b*) with the maximum hydrogen-ion concentration?

Problem 26.—Approximately how much potassium glycollate should be added to 1 liter of a 0.02 normal glycolic acid solution in order to give it the same hydrogen-ion concentration as a 0.02 normal cumic acid solution?

B. HETEROGENEOUS SYSTEMS AT CONSTANT TEMPERATURE

7. The General Equilibrium Law.—Whenever any molecular species which takes part in a chemical equilibrium in a system at a constant temperature and under a constant external pressure is represented in that system by a pure crystalline phase, then the vapor pressure or fugacity of that molecular species cannot be changed by any displacement of the chemical equilibrium, for the pressure of the vapor of any substance in equilibrium with its pure crystals can have only one value at a given temperature and pressure. (Cf. VI, 1.) In other words, if the substance A is involved in any chemical equilibrium in a gas or solution, then as long as the gas or solution is kept in contact with and in equilibrium with crystals of A, the value of the coefficient $\left(\frac{\partial p_A}{\partial x}\right)_{T,P}$, is equal to zero. (Cf. XXII, 3*a*.) Owing to the very small value of the ratio, $\frac{V_0}{v_0}$, for crystals at moderate pressures, it follows from equation (7, XII) that the coefficient $\left(\frac{\partial p_A}{\partial P}\right)_T$ must also be extremely small under these conditions. Hence the quantity, $dp_A = \left(\frac{\partial p_A}{\partial x}\right)_P dx + \left(\frac{\partial P_A}{\partial P}\right)_x dp$, which appears in the general law governing chemical equilibrium (equation 4) is either zero or is negligibly small, if the substance A is present in the system as a pure crystalline phase. We thus reach the conclusion that for a chemical equilibrium in a heterogeneous system, not only the general thermodynamic law governing the equilibrium but also all the special integrated forms of it (such as equations 7, 8, 10, 11, and 13) are identical with the corresponding equations for homogeneous systems, but *with the omission of all terms referring to substances present in the system as pure crystalline phases.* It is clear that this same statement would also hold true for any substances which were present as pure liquids or whose fugacities were kept constant by any means whatsoever.

8. Crystals in Equilibrium with Gases.—From the general conclusion deduced in the preceding section it is evident that for the equilibrium represented by the equation (Cf. XIX, 1)

$$\underline{\mathrm{NH_4Cl}} \rightleftharpoons \overline{\mathrm{NH_3}} + \overline{\mathrm{HCl}}$$

in which crystalline ammonium chloride is in equilibrium with its gaseous dissociation products, the equilibrium law would be

$$p_{\mathrm{NH_3}} \cdot p_{\mathrm{HCl}} = \mathrm{const.} = K_p \tag{26}$$

and

$$C_{\mathrm{NH_3}} \cdot C_{\mathrm{HCl}} = \mathrm{const.} = K_c \tag{27}$$

corresponding to the general equations (7) and (8).

Problem 28.—Formulate the equilibrium laws of the following reactions:

$$\underline{\mathrm{CaCO_3}} = \underline{\mathrm{CaO}} + \overline{\mathrm{CO_2}} \tag{28}$$

$$3\underline{\mathrm{Fe}} + 4\overline{\mathrm{H_2O}} = \underline{\mathrm{Fe_3O_4}} + 4\overline{\mathrm{H_2}} \tag{29}$$

$$\mathrm{BaCO_3}aq + \underline{\mathrm{SrSO_4}} = \underline{\mathrm{BaSO_4}} + \mathrm{SrCO_3}aq \tag{30}$$

$$\underline{\mathrm{PbO}} + \underline{\mathrm{NH_4Cl}} = \underline{\mathrm{Pb(OH)Cl}} + \overline{\mathrm{NH_3}} \tag{31}$$

$$\underline{\mathrm{NH_4OCONH_2}} = 2\overline{\mathrm{NH_3}} + \overline{\mathrm{CO_2}} \tag{32}$$

$$\underline{\mathrm{C}} + \overline{\mathrm{CO_2}} = 2\overline{\mathrm{CO}} \tag{33}$$

$$\underline{\mathrm{Fe_2O_3}} + 3\overline{\mathrm{CO}} = 2\underline{\mathrm{Fe}} + 3\overline{\mathrm{CO_2}} \tag{34}$$

The equilibrium constants for the above reactions have all been experimentally determined. The principal features of an apparatus for determining the value of the equilibrium constant for reaction (29) are illustrated in Fig. 40. The air is first completely pumped out of the apparatus and the granular mixture of solid $Fe+Fe_3O_4$ in the horizontal reaction tube is heated electrically to the desired temperature. After equilibrium is attained the total pressure inside the apparatus is registered by the manometer. This pressure is equal to the partial pressure of the hydrogen produced by the reaction plus the partial pressure of the water vapor. This latter pressure is kept constant owing to the presence in the apparatus of liquid water at a definite temperature which can be controlled by means of a constant temperature bath into which the whole apparatus is plunged.

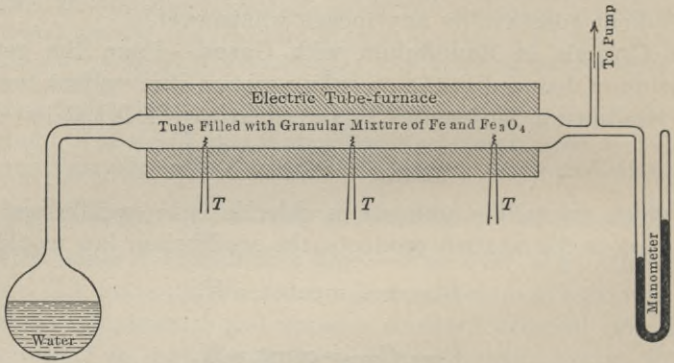


FIG. 40.—Illustrating the principal features of an apparatus for determining the equilibrium constant for the reaction $\underline{3Fe}+4\overline{H_2O}=\underline{Fe_3O_4}+4\overline{H}_2$. *T* indicates thermocouples for measuring the temperature inside the reaction tube. Experiments with this apparatus are described by G. Preuner, Z. physik. Chem., **47,** 392 (1904).

Problem 29.—In one experiment with the apparatus shown in Fig. 40, the constant temperature bath surrounding the whole apparatus was maintained at 38° and the reaction tube at 900°. When equilibrium had been reached the manometer registered 121 mm. The vapor pressure of water at 38° is 49.7 mm. Calculate the equilibrium constant for reaction (29) at 900°. If the constant temperature bath had been regulated at 20° instead of 38° in the above experiment what would the manometer have read after the attainment of equilibrium? (See IV, 1, Table IX.)

(The mean value obtained experimentally under these conditions was 43.7 mm.)

9. Crystals in Equilibrium with Solutions.—On the basis of the reasoning given in section 7 above, the student should have no difficulty in formulating the equilibrium expression for any heterogeneous chemical equilibrium in a solution of constant thermodynamic environment.

Problem 30.—When phenanthrene picrate is dissolved in alcohol it dissociates partially into free phenanthrene and free picric acid. Assuming that the thermodynamic environment within the solution remains constant, formulate the equilibrium law for the above reaction when the solution is kept saturated (1) with picric acid; (2) with phenanthrene; (3) with the solid salt; (4) with both the solid salt and the acid.

Aqueous solutions saturated with crystalline electrolytes form an important group of heterogeneous equilibria in solutions whose thermodynamic environment is a function of the ion concentration. Take for example the equilibrium represented by the equation

$$\underline{CA} \rightleftharpoons C^+ + A^-$$

where a solution is saturated with the solid uni-univalent electrolyte, CA. As explained in section 7 above, the general thermodynamic law for this equilibrium (equation 7) becomes

$$p_{C^+} \cdot p_{A^-} = \text{const.} \tag{35}$$

where p represents the fugacity of the ion species indicated.

In order to obtain a relation involving the *concentrations* of the two ion species in the solution, it is only necessary to know the relation between fugacity and concentration for each ion-species. We have already seen (XVII, 6*b*) that the fugacity of an ion-species, while approximately proportional to its concentration, increases rather more slowly than the latter. This may be conveniently expressed by the relation

$$p_i = kC_i - \mathrm{f}_i(C_i) \tag{36}$$

where $\mathrm{f}_i(C_i)$ is small in comparison with kC_i. If we combine an equation of this form for each ion species (C^+ and A^-) with equation (35) above, we have

$$[C^+][A^-] = \text{const.} + \mathrm{f}(C_i) \tag{37}$$

in which $\mathrm{f}(C_i)$ is a positive quantity small in comparison with the const. term. For many purposes the term $\mathrm{f}(C_i)$ may be neglected in comparison with the constant and we may write equation (37) in the following approximate form:

$$[C^+]\,[A^-] = \text{const.} = (\alpha_0 S_0)^2 \tag{38}$$

where S_0 is the solubility of the salt in pure water and α_0 its degree of ionization in this saturated solution. The validity of equation (38) can be tested by experiment. Suppose we have a saturated solution of the slightly soluble salt, TlCl. By additions of KCl and of $TlNO_3$ respectively to this solution we can vary the values of $[Tl^+]$ and $[Cl^-]$ in this solution through wide limits and can thus discover whether or not their product remains constant as required by equation (38).

Experiments of this character have been carried out with a number of electrolytes and the conclusions reached may be summed up as follows: *In sufficiently dilute solutions saturated with a slightly soluble uni-univalent salt the product of the concentrations of the ion species of that salt is constant.* This statement, which is expressed mathematically by equation (38), is usually known as the **solubility-product law.** It is more nearly true the less soluble the salt and the more dilute the solution. For most purposes it holds sufficiently well for all cases where the solubility of the salt and the ion concentration of the solution are both not more than a few hundredths of an equivalent per liter. An example illustrating the accuracy with which the principle holds for a specific case is shown in Fig. 41. This figure is based upon measurements made by Bray and Winninghof[7] with solutions of thallous chloride at 25°. The solubility of this salt in pure water at 25° is 0.01629 equivalents per liter. Its solubility in solutions of $TlNO_3$, KCl and KNO_3 of varying strengths was determined and the values of the solubility product $[Tl^+]\ [Cl^-]$ in these different solutions were calculated with the aid of the isohydric principle and are plotted as ordinates in the figure, corresponding values of the total-ion concentration of the solution, raised to the $\frac{1}{2}$ power ($C_i^{\frac{1}{2}}$), being plotted as abscissæ.

It is evident from this figure that the solubility product for this salt is *not constant*, but increases regularly as the total-ion concentration of the solution increases, being in fact approximately a linear function of $C_i^{\frac{1}{2}}$. That is, the solubility product for this salt may be conveniently expressed by an equation of the form

$$[C^+]\ [A^-] = k + k'C_i^h \tag{39}$$

where h is approximately $\frac{1}{2}$ and the constants k and k' depend upon the nature of the ion species present in the solution. This equation has the same form as the Kraus equation, equation (20), for the ionization of strong electrolytes. The straight lines drawn in Fig. 41 are graphs of the equations indicated on the figure. Although the solubility product very evidently increases as the total-ion concentration increases, the change is not very rapid and for ion concentrations not greater than 0.04 (*i.e.*, $C_i^{\frac{1}{2}} = 0.2$) the solubility product for thallous chloride may evidently be taken as constant within 10 per cent. For less soluble salts the magnitude of the solubility product and its rate of change with the ion concentration are both much smaller.

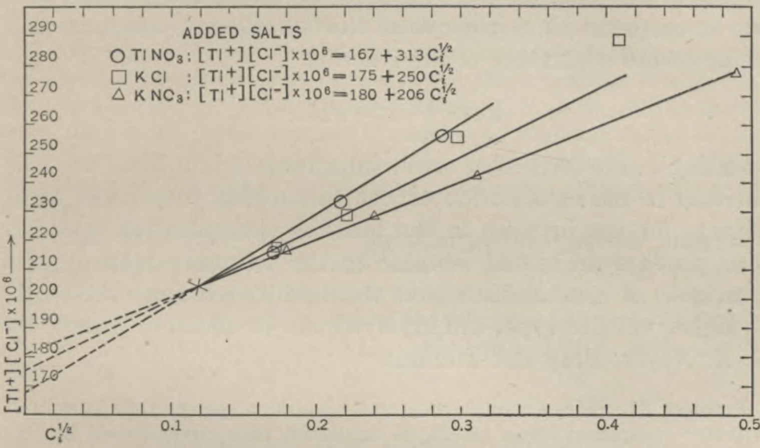


Fig. 41.—Illustrating the variation of the solubility product $[Tl^+]$ $[Cl^-]$ in solutions saturated with thallous chloride and containing respectively the salts $TlNO_3$, KCl, and KNO_3 at different concentrations. The point marked by the cross represents the value for a pure aqueous solution of thallous chloride. The total ion concentration for each solution is calculated by means of the isohydric principle. This figure is based upon experimental data obtained by Bray and Winninghof at 25°.

The application of the solubility product law to salts of higher valence types (XV, 3*b*) or to salts of any valence type when the solution contains a salt of a higher valence type is complicated by the presence of intermediate ions (XVII, 3) whose concentrations and equilibrium relations are not known. Thus, for example, the solubility product law for a solution saturated with $PbCl_2$ would read

$$[Pb^{++}]\ [Cl^-]^2 = \text{const.} \qquad (40)$$

and if either the chloride-ion concentration or the lead-ion concentration of the solution were increased by the addition of a salt with the common ion, we should expect the solubility of the $PbCl_2$ to be diminished. This is what actually happens when a chloride, such as KCl, is added to a saturated solution of $PbCl_2$. When, however, a salt ($Pb(NO_3)_2$, for example) having the common bivalent ion is added, the solubility of the $PbCl_2$ may actually be *increased*. The addition of the $Pb(NO_3)_2$ doubtless increases the lead-ion concentration of the solution somewhat, but at the same time it *decreases* the chloride-ion concentration owing to the occurrence of the reaction

$$Pb^{++} + Cl^- = PbCl^+$$

resulting in the formation of the intermediate ion, $PbCl^+$. This decrease in the chloride-ion concentration may more than compensate for the increase in the lead-ion concentration and can thus produce an actual increase in the solubility instead of a decrease. A general discussion of solubility relations when salts of higher valence types are involved can be found in papers[8] by A. A. Noyes, Bray and Harkins.

Problem 31.—When conductivity water having a specific conductance of $0.70 \cdot 10^{-6}$ reciprocal ohms at 18° is saturated with silver iodate at this temperature, the specific conductance of the saturated solution is found to be 12.6×10^{-6} reciprocal ohms. Calculate the solubility product $(\alpha_0 S_0)^2$ for $AgIO_3$ at 18°.

Problem 31 shows that with the aid of conductance measurements it is possible to determine the solubility product $(\alpha_0 S_0)^2$ without knowing either the solubility (S_0) itself or the degree of ionization (α_0) in the saturated solution.

Problem 32.—From the value of $\alpha_0 S_0$ obtained in problem 31 compute the solubility of silver iodate at 18°, first under the assumption that its degree of ionization in the saturated solution is the same as that of potassium iodate at the same concentration, and second under the assumption that it is the same as that of silver nitrate at the same concentration.

Problem 33.—From the results of the preceding problems calculate the solubility, S, of $AgIO_3$ (*a*) in a 0.01 molal solution of $AgNO_3$ and (*b*) in a 0.02 molal solution of KIO_3 at 18°.

Problem 34.—From the results of the preceding problems calculate the amount of $AgIO_3$ which will dissolve in a 0.02 formal solution of NH_3 at 18°, assuming that the complex ion, $Ag(NH_3)_2^+$, forms quantitatively. (Cf. XV, problem 5 and XVIII, problem 13.)

Problem 35.—The solubility of silver chloride in water at 25° is 2 mg. per liter. If a precipitate of AgCl is washed with 2 liters of wash water at 25°, how much $AgNO_3$ should the wash water contain in order to prevent the dissolving of more than 0.05 mg. of AgCl during the operation of washing? Assume equilibrium to be established during the washing.

Problem 36.—The solubility of thallous chloride is 0.0163 and that of thallous sulphocyanate 0.0149 mole per liter. How many grams of thallium can be obtained from 1 liter of a solution which is saturated with both salts at the same time?

Problem 37.—State and interpret in the light of the facts presented in this chapter the effect on the solubility of cuprous iodide (CuI) produced by the presence of the following substances in *dilute* aqueous solution: (1) Cuprous chloride, (2) iodine, (3) cupric sulphate, (4) NH_3, (5) lithium nitrate, (6) a strong oxidizing agent, (7) sugar, (8) potassium iodide, (9) hydrochloric acid, (10) acetic acid. State also, as far as possible, the relative magnitudes of the effects of the above substances. (See equation 74, XXIII.)

Problem 38.—What would be the direction and relative magnitude (whether large or small) of the effects on the solubility of silver benzoate ($S_0 = 0.014$ mole per liter) produced by adding separately to 1 liter of a saturated solution 0.05 mole of each of the following substances? Explain what occurs in each case. $AgClO_3$, C_6H_5COOLi, $LiNO_3$, NH_3, LiCN, HNO_3, HCl. Benzoic acid is a weak acid.

C. TEMPERATURE AND CHEMICAL EQUILIBRIUM

10. The General Thermodynamic Law.—If A is the increase in free energy (X, 9 and 11) which is associated with the occurrence of a chemical reaction at a constant temperature T, then it follows from the Second Law of thermodynamics, as formulated in equation (10, X), that this free energy changes with the temperature at a rate which is expressed by the equation

$$\frac{\mathrm{d}A}{\mathrm{d}T} = \frac{Q}{T} \tag{41}$$

For the chemical equilibrium, $a\mathrm{A} + b\mathrm{B} + \ldots . \rightleftarrows m\mathrm{M} + n\mathrm{N} + \ldots .$, in the gaseous state at constant pressure this rate can be shown (Appendix, 15) to be

$$\left(\frac{\partial A}{\partial T}\right)_P = \left(\frac{mv_\mathrm{M}\partial p_\mathrm{M} + nv_\mathrm{N}\partial p_\mathrm{N} + \ldots - av_\mathrm{A}\partial p_A - bv_\mathrm{B}\partial p_\mathrm{B} - \cdots}{\partial T}\right)_P \tag{42}$$

where p_{M} is the partial pressure of M, v_{M} is its molal volume, and similarly for the other substances. Combining this relation with equation (41) above gives (see equations 4 and 5)

$$\left(\frac{\Sigma m v_{\mathrm{M}} \partial p_{\mathrm{M}}}{\partial T}\right)_P = \frac{H_P}{T} \tag{43}$$

where H_P, the heat-of-the-reaction (XIX, 5), is the heat *evolved* when the reaction as written takes place, *at constant pressure, from right to left,* that is, so as to produce the substances A and B.

If the substances involved in the equilibrium are all perfect gases, then as explained in section 3*a* above,

$$\Sigma m v_{\mathrm{M}} \partial p_{\mathrm{M}} = RT \partial \log_e \frac{p_{\mathrm{M}}^m \cdot p_{\mathrm{N}}^n \cdots}{p_{\mathrm{A}}^a \cdot p_{\mathrm{B}}^b \cdots} = RT \partial \log_e K_p \tag{44}$$

and equation (43) may be written

$$\frac{\mathrm{d} \log_e K_p}{\mathrm{d}T} = \frac{H_P}{RT^2} \tag{45}$$

an equation which expresses the dependence of the equilibrium constant, K_p, upon the temperature. H_P, the heat-of-the-reaction at constant pressure, is evidently the heat *evolved* when the reaction takes place at constant pressure in such a direction that the *products* of the reaction are those substances which appear in the *denominator* of the equilibrium expression, K_p.

If we formulate the equilibrium expression in terms of concentrations instead of partial pressures (*i.e.*, employ equation (8) instead of equation (7)), then it follows from the relation connecting K_p with K_c and the relation connecting H_p with ΔU (equations (36) and (40), XIX) that

$$\frac{\mathrm{d} \log_e K_c}{\mathrm{d}T} = \frac{\Delta U}{RT^2} \tag{46}$$

where ΔU, the increase in total energy which accompanies the reaction, is equal to the heat *evolved* when the reaction takes place *at constant volume* in such a direction that the *products* of the reaction are the substances which appear in the *denominator* of the equilibrium expression, K_c.

Problem 39.—Deduce equation (46) in the manner indicated.

Equations (45) and (46) also hold for heterogeneous equilibria involving gases. Thus for the equilibrium, $a\overline{\mathrm{A}}+b\underline{\mathrm{B}}+c\overline{\mathrm{C}}\rightleftharpoons m\overline{\mathrm{M}}+n\underline{\mathrm{N}}$, we would write (Sec. 7)

$$\frac{C_{\mathrm{M}}^{m}}{C_{\mathrm{A}}^{a}\cdot C_{\mathrm{C}}^{c}}=K_c \tag{47}$$

and ΔU would be the heat *evolved* when n moles of the substance N in the crystalline state reacted with m moles of the substance M in the gaseous state to produce a moles of the substance A and c moles of the substance C, both in the gaseous state, and b moles of the substance B in the crystalline state.

By reasoning similar to the above (Appendix, 16), we can show that for equilibria (whether homogeneous or heterogeneous) in solutions of constant thermodynamic environment we have the relation

$$\frac{\mathrm{d}\log_e K_x}{\mathrm{d}T}=\frac{\Delta U}{RT^2} \tag{48}$$

which for dilute solutions assumes the form (see equations 12 and 13)

$$\frac{\mathrm{d}\log_e K_c}{\mathrm{d}T}=\frac{\Delta U}{RT^2} \tag{49}$$

where ΔU is the heat *evolved* when the reaction in the solution at T^0 and in constant thermodynamic environment takes place without the production of external work in such a direction as to produce the substances which appear in the *denominator* of the equilibrium expression. Equation (49) is known as the van't Hoff equation.

Problem 40.—When water vapor is heated to high temperatures it dissociates partially into hydrogen and oxygen according to the equation

$$2\mathrm{H_2O}=2\mathrm{H_2}+\mathrm{O_2} \tag{50}$$

and the equilibrium constant for this reaction at 1227° is

$$\frac{p_{\mathrm{H_2}}^{2}\cdot p_{\mathrm{O_2}}}{p_{\mathrm{H_2O}}^{2}}=K_p=4.12\cdot 10^{-12} \tag{51}$$

At 0° we have also the thermochemical equation

$$\overline{\mathrm{H_2}}+\overline{\mathrm{O_2}}=\overline{\mathrm{H_2O}}+57{,}510 \text{ cals.} \tag{52}$$

(*a*) Calculate H_P for reaction (50) at 0°. H_P for this reaction varies with the temperature according to the equation

$$\frac{\mathrm{d}H_p}{\mathrm{d}T} = -0.94 - 0.0033T + 0.00000222T^2 \qquad (53)$$

(*b*) From these data calculate the value of K_p for this reaction at 2227°. (*c*) Calculate K_c at 1227° and at 2227°. (*d*) Calculate the degree of dissociation of water at each temperature under a pressure of 1 atmosphere. (*e*) If 0.1 mole of H_2O in a vessel of 10 liters capacity be heated to 2227°, how many moles of oxygen will be produced? (*f*) How many if the vessel has a capacity of 100 liters?

Problem 41.—From the data given in problem 13 calculate the value of H_v in the thermochemical equation

$$\underline{NH_4Cl} = \overline{NH_3} + \overline{HCl} + H_v \qquad (54)$$

Calculate the sublimation pressure of NH_4Cl at 306°.

Problem 42.—Prove that the temperature coefficient $\left(\frac{1}{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)$ of the degree of ionization of a weak electrolyte in dilute solution is expressed by the equation

$$\frac{1}{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{-H_v(1-\alpha)}{RT^2(2-\alpha)} \qquad (55)$$

where H_v, the heat-of-ionization, is the heat evolved during the ionization of one mole of the electrolyte. From data obtainable in problems 7 and 8, Chapter XIX, and Tables XX and XXI, Chapter XVII, calculate the percentage rate at which the degree of ionization of a 0.05*n* solution of acetic acid changes with the temperature at 18°. On the assumption that H_v is independent of T calculate with the aid of equation (55) the degree of ionization of a 0.05*n* solution of acetic acid at 25° and compare your results with the value obtained in problem 20 above.

Problem 43.—By determining the solubility (S_0) of orthonitrobenzoic acid in water at different temperatures Noyes and Sammet[9] found that for this substance $\left(\frac{\mathrm{d}\log_e S_0}{\mathrm{d}T}\right)_{20^\circ} = 0.03335$, and from conductance measurements they found similarly $\left(\frac{\mathrm{d}\log_e \alpha}{\mathrm{d}T}\right)_{20^\circ} = -0.0216$. Calculate the value of H_v in the thermochemical equation

$$H^+ + B^- = \underline{HB} + H_v \qquad (56)$$

where HB is written for orthonitrobenzoic acid and B^- for its anion. The value of H_v for this reaction, determined calorimetrically, is 4040 ± 100 cal.

11. The Theorem of LeChatelier.—The effect on any physicochemical equilibrium, produced by an attempt to alter any one of the factors which influence it, can be qualitatively predicted by means of a theorem formulated by LeChatelier[a] which may be stated as follows: If an attempt is made to alter any one of the factors (*e.g.*, the temperature or pressure of the system or the fugacity of any constituent of the system) which influence any physico-chemical equilibrium, then a shift in the equilibrium will take place in such a direction as to decrease the magnitude of the alteration which would otherwise occur in that factor.

For example, if we add a certain amount of heat to any system, this will increase the molecular energy of the system and produce a corresponding rise in temperature, but if a physico-chemical equilibrium exists within the system, this equilibrium will be displaced in the direction in which heat is absorbed, and since part of the heat added to the system is used up in this process the increase in the temperature will be smaller than would otherwise be the case. It therefore follows that increase in temperature always displaces an equilibrium in the direction in which heat is absorbed. In a similar way it is evident that increase of pressure will displace an equilibrium in the direction of the smaller volume.

In the case of a chemical equilibrium, if the fugacity of any substance involved in the equilibrium be increased by increasing its mole fraction, then the chemical equilibrium will be displaced in the direction which results in the disappearance of some of this substance. If, however, the fugacity of some inert substance not directly concerned in the chemical equilibrium (*e.g.*, argon in a gaseous mixture, or the solvent in a dilute solution) be momentarily increased by increasing its mole fraction, then the equilibrium will be displaced in the direction of the larger number of molecules, for by this increase in the total number of molecules the mole fraction, and hence also (in most cases) the fugacity, of the inert substance will not undergo so great a permanent increase as would be the case if no shift in equilibrium took place.

Problem 44.—With the aid of the theorem of LeChatelier predict as far as possible the direction in which the equilibrium will be shifted (1) by increasing the external pressure at constant temperature and composition and (2) by adding a large quantity of some inert substance keeping the temperature and external pressure constant, in the case of the reactions

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[a] Henri Louis LeChatelier. Professor of Chemistry in the University of Paris. Member of the Institute of France.

shown in equations (15, 16*a*, 28, 29, 31, 32, 33 and 34) of this chapter. How would you ascertain with the aid of LeChatelier's theorem the effect of increased pressure upon the melting point of a substance? In which direction will the following equilibria be displaced by increasing the temperature?

$$2H_2+O_2 \leftrightarrows 2H_2O$$
$$CO+O \rightleftarrows CO_2$$

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CHAPTER XXIII

CHEMICAL EQUILIBRIA INVOLVING THE IONS OF WATER

1. Scope of the Chapter.—From a purely practical point of view, if for no other reason, aqueous solutions are of more interest to the chemist than almost any other class of solutions with which he has to deal, because in most of the operations which the chemist carries out in solution, water is the solvent which he employs. We have already learned (XVI, 4*b*) that water is itself ionized to a very slight extent into hydrogen ions and hydroxyl ions, and although the number of these ions is so small that pure water is, in fact, a fair electrical insulator, the rôle which they play in many of the processes with which the chemist has to deal is nevertheless of the greatest importance, so important, in fact, that unless it is clearly understood many of the most common everyday operations of the laboratory cannot be intelligently carried out.

The hydrolysis of salts and other substances, the proper use of indicators in titrametric analysis, the proper conditions for precipitation in gravimetric analyses, the catalytic action of water, the maintenance of neutrality, the dissolving of substances, the percentage yield and the character of the products in many industrial processes are all examples of instances in which the part played by the ions of water is frequently of the most fundamental character. In the present chapter we shall consider in some detail a few of these instances in order to illustrate the application of the laws of chemical equilibrium in this important field and to give the student an opportunity to gain some facility in the application of these laws to specific cases.

2. Definitions.—With respect to their ionization products in aqueous solution, electrolytes are classified as acids, bases or salts in accordance with the following definitions:

(*a*) Any electrolyte which gives hydrogen-ion (H^+) as one of the direct products of its ionization is called an **acid.** The extent to which it ionizes in this way is a measure of its strength as an acid.

(*b*) Any electrolyte which gives hydroxyl-ion (OH^-) as one of the direct products of its ionization is called a **base.** The extent to which it ionizes in this way is a measure of its strength as a base.

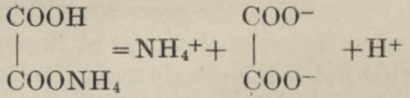
(*c*) An electrolyte which gives at least one positive ion, other than H^+, and at least one negative ion, other than OH^-, as products of its ionization is called a **salt.**

(*d*) A salt may also give hydrogen-ion as one of the direct products of its ionization. It is then an acid as well as a salt and is called an **acid-salt.**

Examples:

$$NaHSO_4 = Na^+ + H^+ + SO_4^{--} \qquad (1)$$

$$K_2HPO_4 = 2K^+ + H^+ + PO_4^{---} \qquad (2)$$



$$\begin{array}{l} COOH \\ | \\ COONH_4 \end{array} = NH_4^+ + \begin{array}{l} COO^- \\ | \\ COO^- \end{array} + H^+ \qquad (3)$$

(*e*) If a salt gives hydroxyl-ion as one of the direct products of its ionization, it is a base as well as a salt and is called a **basic salt.**

Examples:

$$Fe(OH)_2Cl = Fe^{+++} + 2OH^- + Cl^- \qquad (4)$$

$$\underset{\textbf{Potassium glycocollate}}{\underline{CH_2NH_3OH\cdot COOK}} = K^+ + CH_2NH_3OHCOO^-$$

and then

$$CH_2NH_3OHCOO^- = {}^{+}CH_2NH_3COO^- + OH^- \qquad (5)$$

(*f*) Some substances give *both* hydrogen- and hydroxyl-ions as products of their ionization. Such substances are called **amphoteric electrolytes.** Zinc hydroxide is an example of such an electrolyte.

$$Zn(OH)_2 = Zn^{++} + 2OH^- \qquad (6)$$

and

$$H_2ZnO_2 = H^+ + HZnO_2^- \qquad (7)$$

Aluminium hydroxide is another example:

$$Al(OH)_3 = Al^{+++} + 3OH^- \qquad (8)$$

and

$$H_3AlO_3 = H^+ + H_2AlO_3^- \qquad (9)$$

or

$$HAlO_2 = H^+ + AlO_2^- \qquad (10)$$

The formula H_3AlO_3 differs from the formula $HAlO_2$ only by one molecule of H_2O. Since we do not know the degree of hydration of these substances in solution, it is frequently customary to write their formulas without any extra water attached to them, that is, $HAlO_2$ is written in preference to H_3AlO_3 or H_5AlO_4 or H_7AlO_5, etc. It may be that molecules corresponding to each of the above formulas are present in the solution. Similarly we might write the formula of the base AlOOH instead of $Al(OH)_3$. As a base, aluminium hydroxide forms with acids the neutral aluminium salts, such as $AlCl_3$, and basic salts, such as $Al(OH)_2Cl$, which latter salt might equally well be written AlOCl and called aluminyl chloride. As an acid, aluminium hydroxide forms with bases salts called aluminates (*e.g.*, $KAlO_2$). In a similar way zinc hydroxide forms the zinc salts ($ZnCl_2$) and the zincates ($KHZnO_2$).

Amphoteric electrolytes must evidently have *two* ionization constants, one, K_A, for the ionization as an acid and the other, K_B, for the ionization as a base. Thus, for the ionization of arsenous acid $HAsO_2$ (or arsenyl hydroxide, AsOOH) we have for the acid dissociation

$$HAsO_2 = H^+ + AsO_2^- \qquad (11)$$

and

$$\frac{[H^+][AsO_2^-]}{[\Sigma HAsO_2]} = K_A = 6 \cdot 10^{-10} \text{ (at } 25°) \qquad (12)$$

and for the basic dissociation

$$AsOOH = AsO^+ + OH^- \qquad (13)$$

and

$$\frac{[AsO^+][OH^-]}{[\Sigma HAsO_2]} = K_B = 5 \cdot 10^{-15} \text{ (at } 25°) \qquad (14)$$

The quantity $[\Sigma HAsO_2]$ in the above equations is used to represent the *total concentration* of the un-ionized substance. That is,

$[\Sigma HAsO_2]$ means $[AsOOH]+[As(OH)_3]+[HAsO_2]+[H_3AsO_3]+$ etc., the summation including all the different forms in which arsenous arsenic exists in the solution as neutral molecules containing only one atom of arsenic per molecule. The number of different kinds of such molecules present in the solution is not known, but since they are all in chemical equilibrium with one another the mass action law requires that the concentration of any one kind must be proportional to the concentration of every other kind. This being the case, it follows from the principles of proportion that the concentration of any one species must also be proportional to the sum of the concentrations of all the species and we may therefore employ this sum in formulating the equilibrium expression for the ionization reaction, instead of employing the concentration of some one species. From equations (12) and (14) it is evident that arsenous acid is a stronger acid than it is a base. As an acid it forms the arsenites ($KAsO_2$) and as a base, the arsenyl salts ($AsOCl$).

(*g*) Any aqueous solution in which $[H^+]>[OH^-]$ is said to be *acid.* If $[OH^-]>[H^+]$, the solution is said to be *alkaline.* If $[H^+]=[OH^-]$ the solution is said to be *neutral.* The concentration $[H^+]$ of hydrogen-ion in any solution may be called the *true acidity* of that solution and the concentration $[OH^-]$ of hydroxyl-ion in that solution, the *true alkalinity* of the solution.

3. The Ionization of Water.—Every aqueous solution contains both hydrogen-ion and hydroxyl-ion owing to a slight ionization of the water itself according to the equation

$$H_2O=H^++OH^- \tag{15}$$

Water is therefore both an acid and a base, but since H^+ and OH^- must evidently be produced in exactly equivalent amounts, its strength as an acid must be equal to its strength as a base and pure water must, according to the above definitions, be neutral.

The mass action law for the ionization of water gives, in terms of fugacities (XXII, 3*b*),

$$\frac{p_{H^+}\cdot p_{OH^-}}{p_{H_2O}}=\text{const.} \tag{16}$$

Now the partial vapor pressure of water from dilute aqueous solutions is not greatly different from the vapor pressure of pure water. For example, the vapor pressure of water is changed less than 1.5 per cent. by dissolving enough KCl to form a 0.5*n* solution. (See XV, 2.) For dilute aqueous solutions (say up to 0.1 molal) we may, therefore, write $p_{H_2O} = \text{const.}$ without introducing an error as great as 1 per cent. Equation (16) may then be written

$$p_{H^+} \cdot p_{OH^-} = \text{const.} \tag{17}$$

and, if we assume that the fugacity of each ion-species is proportional to its concentration (XVII, 6*b*), we have

$$[H^+][OH^-] = K_w \tag{18}$$

or stated in words: In any dilute aqueous solution the product of the concentrations of H^+-ion and OH^--ion in that solution is always equal to a constant quantity, K_w, whose value depends only upon the temperature. K_w is called *the ionization constant of water*. Values of $K_w \cdot 10^{14}$ for different temperatures are shown in the following table:

TABLE XXVIII

The Ionization Constant of Water at Different Temperatures

$t°$	0	18	25	50	75	100	128	136	218	306
$K_w \cdot 10^{14}$	0.09	0.5	1.0	4.5	16.9	48	114	220	461	166

Problem 1.—The specific conductance of perfectly pure water as determined by Kohlrausch and Heydweiller at 18° is $0.0384 \cdot 10^{-6}$ reciprocal ohms. With the aid of Table XXI calculate the ionization constant of water at 18°. Calculate also the true acidity and the true alkalinity of pure water at 18°.

Problem 2.—From the values of K_w at 0° and 50° respectively, as given in Table XXVIII, calculate the average value for the heat of ionization of water within this range. Compare your result with equation (35, XIX) and explain.

4. Hydrolysis of Salts. (*a*) **One Constituent Weak.**—If the salt BA of the strong base BOH and the weak acid HA be dissolved in water, it first ionizes

$$BA = B^+ + A^- \tag{19}$$

giving A^--ion. There is always present H^+-ion, also, owing to the ionization of the water, and we thus have present together the two ions, H^+ and A^-, of the weak acid HA, and since in any solution containing these two ions the relation

$$\frac{[H^+][A^-]}{[HA]}=K_A \tag{20}$$

must be satisfied, it is evident that a certain amount of un-ionized acid HA must be formed by the reaction

$$H^+ + A^- = HA \tag{21}$$

The removal of hydrogen-ion from the solution by this reaction, however, disturbs the equilibrium

$$H_2O = H^+ + OH^- \tag{22}$$

and some more water must ionize in order to maintain the product, $[H^+][OH^-]$, constant. We can express these three reactions conveniently in one equation by combining equations (19), (21), and (22), giving us

$$(B^+ + A^-) + H_2O = (B^+ + OH^-) + HA \tag{23}$$

or simply

$$A^- + H_2O = HA + OH^- \tag{24}$$

Reaction (23) (or (24)) is known as **hydrolysis** and the salt is said to be *hydrolyzed*. In writing hydrolysis reactions, and indeed all chemical reactions in solution, it will be convenient, for consideration of the equilibria involved, to write all strong electrolytes in the ionized form and all weak electrolytes in the un-ionized form.

From equation (24) it is evident that the hydrolysis of the salt of a strong base and a weak acid makes the solution alkaline since OH^--ion is one of the products of the hydrolysis. A solution of KCN, for example, is strongly alkaline owing to the following hydrolysis reaction:

$$(K^+ + CN^-) + H_2O = (K^+ + OH^-) + HCN \tag{25}$$

The alkalinity of solutions of Na_2CO_3 is due similarly to the reactions

$$CO_3^{--} + H_2O = HCO_3^- + OH^- \tag{26}$$

$$HCO_3^- + H_2O = H_2CO_3 + OH^- \tag{27}$$

and

$$H_2CO_3 = H_2O + CO_2 \tag{28}$$

If the CO_2 is allowed to escape from a sodium carbonate solution, all three of the above equilibria will evidently be driven toward the right and the alkalinity will be increased. The bicarbonate ion, HCO_3^-, is an acid as well as an ion because it ionizes thus

$$HCO_3^- = H^+ + CO_3^{--} \tag{29}$$

to give hydrogen-ion and carbonate ion. This is also true of the intermediate ions of all polybasic acids.

Problem 3.—Write the reactions for the equilibria which exist in a solution saturated with crystals of $CaCO_3$. From these reactions predict the effects on the solubility of $CaCO_3$ produced by adding to the saturated solution a small quantity of (*a*) nitric acid, (*b*) sodium hydroxide, (*c*) carbon dioxide. The ion, HCO_3^-, is an extremely weak acid, very much weaker than carbonic acid, H_2CO_3.

In the case of a salt of a weak base and a strong acid (aniline hydrochloride, for example), the hydrolysis reaction may be written

$$(B^+ + A^-) + H_2O = BOH + (H^+ + A^-) \tag{30}$$

or

$$B^+ + H_2O = BOH + H^+ \tag{31}$$

and the solution becomes *acid* as a result of the hydrolysis.

(*b*) **Both Constituents Weak.**—When the salt of a weak base and of a weak acid is dissolved in water *both* of the ions of the salt unite with the ions of water to form un-ionized molecules of the weak acid and the weak base respectively. The reaction may be represented thus

$$(B^+ + A^-) + H_2O = BOH + HA \tag{32}$$

If the weak acid HA and the weak base BOH are of equal strength (*i.e.*, if $K_A = K_B$), the solution will evidently remain neutral. If the weak acid is stronger than the weak base, the solution will become slightly acid as a result of the hydrolysis, while if the weak base is the stronger, the solution will become slightly alkaline. The hydrolysis of ammonium acetate, for example,

$$(NH_4^+ + Ac^-) + H_2O = NH_4OH + HAc \tag{33}$$

leaves the solution practically neutral because the ionization constants of ammonium hydroxide and acetic acid are almost identical. If the acid and the base are both extremely weak, the salt will be almost entirely hydrolyzed and the solution will contain only the un-ionized molecules of the weak acid and weak base with very few salt molecules. The hydrolysis of a salt is evidently the reverse of the neutralization of an acid by a base.

5. Degree of Hydrolysis.—Hydrolysis always occurs when the salt of a weak acid or a weak base is dissolved in water. The extent to which the hydrolysis takes place depends upon the ionization constants of the acid and base and upon that of the water at the temperature in question, and it can be calculated if these constants are known. The *degree of hydrolysis, h,* is defined as that fraction of the total salt which has undergone hydrolysis. In order to make clear the factors which determine the extent of the hydrolysis we will now derive an expression for h in terms of the ionization constants involved.

(*a*) **One Constituent Weak.**—We will consider first the hydrolysis of the salt of a strong base and a weak acid in a solution prepared by dissolving C_S moles of the salt in enough water to make the volume of the solution 1 liter. C_S will be called the *total concentration* of the salt in the solution. The hydrolysis reaction is

$$(B^+ + A^-) + H_2O = (B^+ + OH^-) + HA \tag{34}$$

The equilibrium equations which must be satisfied in this solution are evidently

$$\frac{[H^+]\,[A^-]}{[HA]} = K_A \tag{35}$$

and

$$[H^+]\,[OH^-] = K_w \tag{36}$$

for the weak electrolytes. We have also the following relations known as condition equations

$$[HA] = hC_S \tag{37}$$

$$[OH^-] = \alpha_B h C_S \tag{38}$$

where α_B is the degree of ionization of the strong base, BOH, in the solution; and

$$[A^-] = \alpha_S(1-h)C_S \tag{39}$$

where α_S is the degree of ionization of the unhydrolyzed portion of the salt, BA, in the solution.

Eliminating $[OH^-]$ from equations (36) and (38) and making the obvious substitutions in equation (35) we have

$$\frac{h^2\alpha_B C_S}{(1-h)\alpha_S}=\frac{K_w}{K_A}=K_H \tag{40}$$

If we had employed a salt of a weak *base* instead of one of a weak acid, the corresponding equation would be similarly

$$\frac{h^2\alpha_A C_S}{(1-h)\alpha_S}=\frac{K_w}{K_B}=K_H \tag{41}$$

where K_B is the ionization constant of the weak base and α_A the degree of ionization of the strong acid in the solution. From these two equations it is evident that the degree of hydrolysis is greater the weaker the acid (or the base), that is, the smaller K_A (or K_B) is. Moreover, since K_w increases rapidly with rise in temperature (see Table XXVIII) and K_A (or K_B) either increases slowly or else decreases, h also increases rapidly with the temperature.

Since the strong base (or strong acid) which results from the hydrolysis has one ion in common with the unhydrolyzed portion of the salt, the ratio $\frac{\alpha_B}{\alpha_S}\left(\text{or } \frac{\alpha_A}{\alpha_S}\right)$ which appears in equation (40) (or (41)) can be computed by means of the principle stated in problem 18, XXII, and, in so far as the approximate principle regarding the degree of ionization of electrolytes of the same type (XVII, 3) holds true, α_A will be equal to α_S and for approximate calculations equations (40) and (41) may be written

$$\frac{h^2 C_S}{1-h}=\frac{K_w}{K_{A\text{ or }B}}=K_H \quad \text{(approx.)} \tag{42}$$

(*b*) **Both Constituents Weak.**—If both the acid and the base are so weak that they obey the law of mass action, we may write the hydrolysis reaction thus

$$(B^+ + A^-) + H_2O = BOH + HA \tag{43}$$

and the following equilibrium equations must be satisfied in the solution

$$\frac{[H^+][A^-]}{[HA]}=K_A \tag{44}$$

$$\frac{[B^+][OH^-]}{[BOH]}=K_B \tag{45}$$

and

$$[\mathrm{H}^+]\,[\mathrm{OH}^-] = K_w \tag{46}$$

These when combined give us

$$\frac{[\mathrm{HA}][\mathrm{BOH}]}{[\mathrm{B}^+][\mathrm{A}^-]} = \frac{K_w}{K_B \cdot K_A} \tag{47}$$

Now one of the constituents, either the acid or the base, will usually be stronger than the other. Let us assume first that the base is the stronger of the two. The solution will, therefore, be somewhat alkaline and we will have the following condition equations:

$$[\mathrm{HA}] = hC_S \tag{48}$$

$$[\mathrm{BOH}] + [\mathrm{OH}^-] = \text{total base} = hC_S \tag{49}$$

$$[\mathrm{A}^-] = \alpha_S(1-h)C_S \tag{50}$$

$$[\mathrm{B}^+] = [\mathrm{A}^-] + [\mathrm{OH}^-] = \alpha_S(1-h)C_S + \alpha_B hC_S \tag{51}$$

Combining these condition equations with equation (47) gives us

$$\frac{h^2}{(1-h)^2\alpha_S{}^2}\left(\frac{1-\alpha_B}{1+\dfrac{h\alpha_B}{(1-h)\alpha_S}}\right) = \frac{K_w}{K_A \cdot K_B} = K_H \tag{52}$$

and

$$\frac{h}{(1-h)\alpha_S} = \sqrt{\frac{K_w}{K_A \cdot K_B}}\sqrt{\frac{1+\dfrac{h\alpha_B}{(1-h)\alpha_S}}{1-\alpha_B}} = \tag{53}$$

For K_B we have from equations (49), (50) and (51) above

$$K_B = \frac{[\mathrm{B}^+][\mathrm{OH}^-]}{[\mathrm{BOH}]} = \frac{(\alpha_S(1-h)C_S + \alpha_B hC_S)(\alpha_B hC_S)}{(1-\alpha_B)hC_S} \tag{54}$$

and if we impose the condition that $\alpha_B \not> p$ per cent., we find for substantially all cases where $h \not> 50$ per cent. that K_B must not exceed $(1-h)C_S\frac{p}{100}$. But if $\alpha_B \not> p$ per cent. and $h \not> 50$ per cent., then it can be seen by inspection that the quantity under the second radical in equation (53) will not differ from unity by more than $2p$ per cent., and hence for an accuracy of p per cent. in K_H we may write equation (53) in the form

$$\frac{h}{(1-h)\alpha_S} = \sqrt{\frac{K_w}{K_A K_B}} = \sqrt{K_H} \quad \text{(approx.)} \tag{55}$$

Equation (55) may, therefore, be used in place of the more complicated equation (53), provided that $h \not> 50$ per cent. and provided also that $K_B \not> (1-h)C_S\frac{p}{100}$. If $h > 50$ per cent., equation (55) may still be employed, if K_B is small enough, the exact condition being evidently that $\frac{2h\alpha_B}{(1-h)} \not> \frac{p}{100}$, where p is the percentage accuracy with which it is desired that K_H be known.

Problem 4.—If the value of K_H is in error by p per cent., what will be the error in the value of h computed from equation (55), when h is equal to (*a*) 90 per cent., (*b*) 50 per cent., (*c*) 10 per cent., (*d*) 1 per cent.?

In using equations (53) and (55) the best procedure is to employ equation (55) first in order to obtain an approximate value for K_H. Then using this approximate value, apply the two criteria given above in order to determine whether the use of equation (55) is justifiable for the case in hand. If this proves not to be the case or if there is any question, the calculation should be repeated with the aid of equation (53). In this repetition it will be sufficiently exact to substitute the approximate value of K_H in place of the expression $\frac{h}{(1-h)\alpha_S}$ where it occurs under the second radical in equation (53). α_B when required can be computed from equation (54).

In all of the above discussion we have assumed that the weak base is stronger than the weak acid. If the reverse is the case, the derivation and discussion are entirely analogous, the final expressions differing from those given above simply in the substitution of the subscript A in place of the subscript B and *vice versa.*

Problem 5.—Derive the relation corresponding to equation (53) for the case that the weak acid is stronger than the weak base and state the conditions under which the equation reduces to the form (55).

By comparing equations (40) and (55) it will be noted that if only one of the constituents of the salt is weak, the degree of hydrolysis is approximately inversely proportional to the square root of the concentration of the unhydrolyzed salt, while if both constituents of the salt are weak, its degree of hydrolysis is nearly independent of its concentration.

Problem 6.—Calculate approximately the degree of hydrolysis of each of the following salts in 0.1 and in $0.01n$ solution respectively, at 25°:

KCy, PyCl, and PyCy. The ionization constants are, for hydrocyanic acid, HCy, $7.2 \cdot 10^{-10}$; for pyridine hydroxide, PyOH, $2.28 \cdot 10^{-9}$. Calculate also the "true acidity" and the "true alkalinity" (XXIII, 1*g*) of each of the above solutions.

6. Experimental Methods for Investigating Chemical Equilibria which Involve the Ions of Water.—The manner in which the degree of hydrolysis of a salt can be calculated from the equilibrium constants involved has just been explained. It is clear that if we could determine the degree of hydrolysis by direct experiment, we might then employ the equations just derived in order to compute the value of K_w or K_A or K_B. We shall now proceed to consider some of the experimental methods which are employed in the measurement of degree of hydrolysis and in studying chemical equilibria in general in aqueous solutions.

(*a*) **The Conductance Method.**—The specific conductance, $\overline{L}$, of any solution containing a number of ions is expressed by the equation

$$1000\overline{L} = \Sigma[\mathrm{X}]\Lambda_{\mathrm{X}} \tag{56}$$

where [X] is the equivalent concentration of the ion-*species*, X, and Λ_{X} is the *equivalent conductance* of that ion-species in the solution. The summation extends over all of the ion-species present. (Problem: Derive this relation. See equation (29), XVI, and equations (2), (3), (4) and (5), XVII.)

The Measurement of Hydrolysis by the Conductance Method.—As an example of the application of the conductance method to the measurement of the degree of hydrolysis of a salt of a strong base and a weak acid, let us consider a solution in which the hydrolysis equilibrium

$$(\mathrm{B^+} + \mathrm{A^-}) + \mathrm{H_2O} \rightleftharpoons (\mathrm{B^+} + \mathrm{OH^-}) + \mathrm{HA} \tag{57}$$

exists. For the specific conductance of this solution we have

$$1000\overline{L} = [\mathrm{B^+}]\Lambda_{\mathrm{B^+}} + [\mathrm{A^-}]\Lambda_{\mathrm{A^-}} + [\mathrm{OH^-}]\Lambda_{\mathrm{OH^-}} \tag{58}$$

(Question: Why is it justifiable to omit the term $[\mathrm{H^+}]\Lambda_{\mathrm{H^+}}$ from this summation?) If we substitute for each ion concentration the expressions given in equations (38) and (39) and solve the resulting expression for h, we obtain

$$h = \frac{1000\overline{L} - C_S\alpha_S(\Lambda_{\mathrm{B^+}} + \Lambda_{\mathrm{A^-}})}{C_S\alpha_B(\Lambda_{\mathrm{B^+}} + \Lambda_{\mathrm{OH^-}}) - C_S\alpha_S(\Lambda_{\mathrm{B^+}} + \Lambda_{\mathrm{A^-}})} \tag{59}$$

We can also write (see equation (29), XVI, and equations (2) to (5), XVII)

$$1000\bar{L}_S = C_S\alpha_S(\Lambda_{B^+} + \Lambda_{A^-}) \qquad (60)$$

and

$$1000\bar{L}_B = C_S\alpha_B(\Lambda_{B^+} + \Lambda_{OH^-}) \qquad (61)$$

where $\bar{L}_S$ is the specific conductance of the *unhydrolyzed* salt when its concentration is C_S, and $\bar{L}_B$ is the specific conductance of a solution of the pure base BOH when its concentration is C_S. Hence

$$h = \frac{\bar{L} - \bar{L}_S}{\bar{L}_B - \bar{L}_S} \qquad (62)$$

Equation (59), with Λ_X taken as equal to Λ_{0_X} for each ion, will give as accurate results as the conductance data justify, if the degree of hydrolysis is not too large. Equation (62) is more reliable but will require more measurements in some cases. For a salt of a strong acid and a weak base equations (59) and (62) also hold, if the subscript B is replaced by A, and OH^- by H^+.

If the salt is one in which *both* the acid and the base are weak, the conductance method is also applicable, but the calculation is in general somewhat more complicated than when only one constituent is weak and we shall not discuss the details of it here. Evidently the conductance method is of practical value only when the change in conductance due to the hydrolysis is large enough to make an accurate determination of its value possible.

Problem 7.—The specific conductance of a 0.001687 normal solution of sodium acetate at 218° is $1.0171 \cdot 10^{-3}$ reciprocal ohms. By adding successive small portions of acetic acid to the solution (the normality of the solution with respect to the salt being kept constant) it was found that its specific conductance could be reduced to $984 \cdot 10^{-6}$ but no further. A 0.001687 normal solution of NaOH has a specific conductance of $1.738 \cdot 10^{-3}$ reciprocal ohms at 218°. Calculate the degree of hydrolysis of the sodium acetate at 218°.

Problem 8.—The great effect of temperature upon degree of hydrolysis will be appreciated by computing the degree of hydrolysis for the above solution at 25°. Look up the necessary ionization constants.

The Determination of the Ionization Constant of a Very Weak Electrolyte.—As a second example of the application of conductance methods to the study of chemical equilibria in solution we will consider the determination of the ionization constant of a very weak base or acid, one which is so weak that the conductance of its own pure solution cannot be measured with sufficient accuracy to determine its ionization constant in the usual way. (See problem 20, XXII.) Suppose we wished to determine the value of K_B for the very weak base BOH.

Let $\bar{L}$ be the specific conductance of a solution of the strong acid HA of concentration C_A equivalents per liter. If we dissolve C_B equivalents of our weak base in 1 liter of the acid solution, the specific conductance of the resulting solution will be $\bar{L}'$, which will be less than $\bar{L}$ owing to the replacement of some of the very mobile hydrogen ions by the less mobile B^+-ions, as a result of the partial occurrence of the neutralization reaction,

$$BOH+(H^++A^-)=(B^++A^-)+H_2O \tag{63}$$

For the solution of the pure acid we have

$$1000\bar{L}=\alpha_A C_A\Lambda_0=[A^-](\Lambda_{H^+}+\Lambda_{A^-})=[H^+](\Lambda_{H^+}+\Lambda_{A^-}) \tag{64}$$

and after the addition of the base we have

$$1000\bar{L}'=[H^+]'\,\Lambda_{H^+}+[A^-]'\Lambda_{A^-}+[B^+]'\Lambda_{B^+} \tag{65}$$

But

$$[H^+]'+[B^+]'=[A^-]' \tag{66}$$

and hence

$$\begin{aligned}1000\bar{L}'&=[A^-]'\Lambda_{H^+}-[B^+]'\Lambda_{H^+}+[A^-]'\Lambda_{A^-}+[B^+]'\Lambda_{B^+}\\&=[A^-]'(\Lambda_{H^+}+\Lambda_{A^-})+[B^+]'(\Lambda_{B^+}-\Lambda_{H^+})\end{aligned} \tag{67}$$

But since the two strong electrolytes, HA and BA, are of the same ionic type and are in solution together they will be ionized to practically the same degree (XXII, 6*e*) in this solution. The occurrence of the neutralization reaction (63) will therefore not produce much change in the concentration of the common ion A^-, and we may write

$$[A^-]=[A^-]' \text{ (approx.)} \tag{68}$$

and on combining equations (68), (67) and (64) we obtain

$$[B^+]'=\frac{1000(\bar{L}-\bar{L}')}{\Lambda_{H^+}-\Lambda_{B^+}} \tag{69}$$

From equations (69), (68), (66) and (64) we find

$$[H^+]'=\frac{1000\bar{L}}{(\Lambda_{H^+}+\Lambda_{A^-})}-\frac{1000(\bar{L}-\bar{L}')}{(\Lambda_{H^+}-\Lambda_{B^+})} \tag{70}$$

which combined with equation (18) gives us

$$[\mathrm{OH}^-]' = \frac{K_w}{[\mathrm{H}^+]'} = \frac{K_w}{\dfrac{1000\bar{L}}{(\Lambda_{\mathrm{H}^+} + \Lambda_{\mathrm{A}^-})} - \dfrac{1000(\bar{L} - \bar{L}')}{(\Lambda_{\mathrm{H}^+} - \Lambda_{\mathrm{B}^+})}} \tag{71}$$

Also

$$[\mathrm{BOH}]' = C_B - [\mathrm{B}^+] = C_B - \frac{1000(\bar{L} - \bar{L}')}{(\Lambda_{\mathrm{H}^+} - \Lambda_{\mathrm{B}^+})} \tag{72}$$

and hence

$$\frac{[\mathrm{B}^+]'[\mathrm{OH}^-]'}{[\mathrm{BOH}]'} = K_{\mathrm{B}} = \frac{\dfrac{1000(\bar{L} - \bar{L}')}{(\Lambda_{\mathrm{H}^+} - \Lambda_{\mathrm{B}^+})} \cdot \dfrac{K_w}{\dfrac{1000\bar{L}}{(\Lambda_{\mathrm{H}^+} + \Lambda_{\mathrm{A}^-})} - \dfrac{1000(\bar{L} - \bar{L}')}{(\Lambda_{\mathrm{H}^+} - \Lambda_{\mathrm{B}^+})}}}{C_B - \dfrac{1000(\bar{L} - \bar{L}')}{(\Lambda_{\mathrm{H}^+} - \Lambda_{\mathrm{B}^+})}} \tag{73}$$

Problem 9.—The specific conductance of 0.1n HCl at 25° is 0.03952 and it is lowered to 0.03886 by dissolving 0.0494 formula weights of $\frac{1}{2}\mathrm{As_2O_3}$ in a liter of the solution. Calculate the value of K_B for the amphoteric electrolyte, arsenous acid. (See XXIII, 1*f*.) Λ_{AsO^+} may be taken as 40 and the other ion-conductances may be computed from Table XXI.

(*b*) **The Colligative Property Method.**—The hydrolysis of a salt having only one weak constituent evidently (see equation 57, above) results in an increase in the concentration of solute molecules in the solution and a consequent lowering of the vapor pressure and the freezing point and an elevation of the boiling point of the solution. If we can measure the change in the magnitude of one of the above properties which results from the hydrolysis, we will have a measure of the increase in solute molecules resulting from the hydrolysis and consequently a measure of the degree of hydrolysis. This method is only applicable to salts of very weak acids or bases (K_{A} or $K_{\mathrm{B}} < 10^{-14}$) where the degree of hydrolysis is fairly large. The details of the method will become evident by the solution of the following problem where freezing-point lowering is the property chosen for measurement.

Problem 10.—A solution prepared by dissolving 0.200 formula weights of KCl in 1000 grams of water has a freezing point of $-0.681°$. If 0.0900 formula weights of $\mathrm{As_2O_3}$ be dissolved in this solution its freezing point is lowered to $-t_1°$. The freezing point of a solution prepared by dissolving 0.2 formula weights of AsOCl in 1000 grams of water is $-t_2°$. On the assumption that $t_1 = 1.010$ and $t_2 = 0.974$, calculate from the above data *alone* the degree of hydrolysis of arsenyl chloride at 0° and 0.2n. Then with the aid of other necessary data calculate the ionization constant of arsenyl hydroxide. When As_2O_3 dissolves in water it reacts thus

$$As_2O_3 + H_2O = \Sigma HAsO_2$$

(See 1*f*, equation (14) above, for the meaning of the formula $\Sigma HAsO_2$.)

(*c*) **The Distribution Method.**—Whenever one of the molecular species concerned in a chemical equilibrium in aqueous solution can be caused to distribute itself between the aqueous solution and some second non-miscible phase in such a way that its concentration in the second phase can be accurately determined, then its concentration in the aqueous solution can evidently be calculated, if the law governing the distribution is known. The following problems illustrate the use of this method, which is of very general application.

Problem 11.—By shaking *successive portions* of a 0.03138*n* solution of aniline hydrochloride, AnCl, with 50 c.c. of benzene at 25° until equilibrium is established, the benzene layer on analysis is found to contain 0.5938 gram of aniline, $C_6H_5NH_2$, per liter. (The value 0.5938 in this experiment is an assumed value.) Assuming that the distribution coefficient of aniline between benzene and a 0.03138*n* aqueous solution of KCl is $\frac{C_B}{C_w} = 10.1$ at 25°, calculate the degree of hydrolysis of the aniline hydrochloride in the water layer and the ionization constant of aniline hydroxide at 25°.

Problem 12.—A current of air is passed through a saturation apparatus made up of a series of tubes containing a solution having the composition 1000 grams of water, 0.002 mole of HCN and enough KCl (about 0.2 mole) to produce the same aqueous tension as that above a 0.2 weight formal solution of KCN. The composition of the solution in the last tube of the saturation apparatus does not change during the experiment. On emerging from the saturation vessel the air passes through an absorption vessel containing a solution of $AgNO_3$. The air thus freed from HCN next passes through a second saturation apparatus just like the first but filled with a 0.2 weight formal solution of KCN, and finally through a second absorption vessel containing a solution of $AgNO_3$. The whole operation is so conducted that the air emerges at practically the same pressure as it enters the system and the whole apparatus is immersed in a constant temperature bath at 50°. If m grams of AgCN are found to have been precipitated in the first absorption vessel and $0.93m$ grams in the second, what is the ionization constant of HCN at 50°?

Problem 13.—When iodine is dissolved in a dilute aqueous solution of any iodide a large part of it combines with the iodide to produce tri-iodide in accordance with the equation,

$$I_2 + I^- = I_3^- \qquad (74)$$

An appreciable quantity, however, remains in solution as I_2-molecules in equilibrium with the iodide and tri-iodide. The distribution constant of I_2-molecules between carbon tetrachloride and a dilute aqueous solution of H_2SO_4 is $\frac{C_{CCl_4}}{C_w}=85$ at 25°. It has been found by experiment at 25° that a solution, prepared by dissolving 0.1622 formula weight of HI and 0.0834 formula weight of I_2 in enough water to form a liter, will be in distribution equilibrium with a 0.112 molal solution of I_2 in CCl_4. Another experiment showed that a solution prepared by dissolving 0.07430 formula weight of HI and 0.001373 formula weight of I_2 in enough water to form a liter was in distribution equilibrium with a 0.00205 molal solution of I_2 in CCl_4. Conductance measurements show that the two acids HI and HI_3 are of equal strengths. (Cf. 1*a*.) From these data compute *two* values for the equilibrium constant of reaction (74) at 25°. (HI and HI_3 are insoluble in CCl_4.)

(*d*) **The Catalytic Method.**—This method is applicable to salts of only one weak constituent and depends upon the fact that the rates of many reactions are catalyzed (XXI, 13) by hydrogen-ion and by hydroxyl-ion, the specific reaction rate being proportional to the concentration of the catalyzing ion. An application of the method has already been illustrated in one instance (problem 8, XXI).

Problem 14.—2100 c.c. of a 7 per cent. cane sugar solution are prepared. This solution is divided into two equal portions, both of which are brought to a temperature of 100°. A 50-c.c. sample of each is removed, cooled to 20°, and its rotation, *R*, determined in a polariscope. To the remainder of one solution 0.1 mole of acetic acid and 0.1 mole of KCl are added and to the other (at the same time) 0.1 mole of aniline hydrochloride (AnCl), and both solutions thoroughly shaken. At measured intervals of time samples are withdrawn from each solution, quickly cooled to 20° (at which temperature the rate of reaction is negligibly small), and polarized. Assume that the following results are obtained in such an experiment.

Solution	HAc+KCl				AnCl			
t, in minutes.....	0	22	40	∞	0	7	15	∞
R, in degrees....	10.66°	2.43°	−0.49°	−3.63°	10.66°	3.19°	− 0.71°	−3.62°

At 100° the ionization constant of acetic acid is $11.1 \cdot 10^{-6}$. Calculate the degree of hydrolysis of 0.1 molal AnCl solution at 100° and the ionization constant of aniline, AnOH, at the same temperature. (See XVII, 4, and Table XXII.) To what extent will aniline acetate be hydrolyzed in 0.1 molal solution at 100°? Why is the KCl added to one portion?

Problem 15.—Outline fully a catalytic method for determining the degree of hydrolysis of potassium orthochlorbenzoate at 50°.

(*e*) **The E.M.F. Method.**—The characteristic electrode potential of the electrochemical reaction

$$\overline{\mathrm{H}}_2-2(-)\rightleftharpoons 2\mathrm{H}^+ \qquad (75)$$

is a function of the hydrogen-ion concentration and of the thermodynamic environment in the solution in contact with the hydrogen electrode (XVI, 4*b*).

Problem 16.—The E.M.F. of the hydrogen electrode in equilibrium with a 0.1 molal solution of aniline hydrochloride at 25° is found to be E volts. By experiment with different solutions containing both NaCl and HCl together, and having a *total* concentration of 0.1 mole per liter, it is found by interpolation that the E.M.F. of the hydrogen electrode in contact with a solution containing $(0.1-a)$ mole of NaCl and a moles of HCl is also E volts. Calculate the degree of hydrolysis of aniline hydrochloride at 25° on the assumption that $a=0.00455$ mole.

(*f*) **The Indicator Method.**—The use of indicators for the purpose of determining the hydrogen-ion concentration of a salt solution is described in section 8, below.

7. Solutions of Constant Hydrogen-Ion Concentration. Reserve Acidity and Reserve Alkalinity.[1]—When a drop of 0.5*n* acid is added to a liter of pure water the hydrogen-ion concentration is increased at once more than 100-fold. Similarly when a drop of 0.5*n* alkali is added the hydroxyl-ion concentration is increased over 100-fold. In other words, pure water possesses no reserve power to neutralize even traces of acids or bases. For this reason the hydrogen-ion concentration of the best distilled water of the laboratory is usually far from being equal to 10^{-7} equivalent per liter at room temperature. It is instead a very uncertain and fluctuating quantity dependent upon the traces of acid or alkaline substances which the water happens to dissolve from the air. For many purposes it is important to have a solution of a definite hydrogen-ion concentration which possesses the power of maintaining its "true acidity" practically without change, even upon additions of strong acids or bases in small quantities. A solution which possesses the power of neutralizing both acids and alkalies and thus of protecting itself against both of them will be said to possess *reserve acidity* and *reserve alkalinity*.

Any solution which contains a weak acid together with its salt or a weak base together with its salt possesses this power. The true acidity of such a solution can be controlled by employing a weak acid or base having the proper ionization constant. The mechanism by which a solution containing a weak acid, HA, and its salt, BA, protects itself against additions of small quantities of acids or bases is through the occurrence of the reactions

$$A^- + H^+ = HA \tag{76}$$

and

$$HA + OH^- = H_2O + A^- \tag{77}$$

by which the added acid or base is neutralized. From these two reactions it is evident that if the reserve acidity and reserve alkalinity are to be equal to each other, then $[A^-]$ should be equal to [HA]. But

$$[H^+] = \frac{[HA]}{[A^-]} K_A \tag{78}$$

and hence

$$[H^+] = K_A \tag{79}$$

or in words, if the reserve acidity and reserve alkalinity are to be equal to each other, then the acid employed should be one whose ionization constant is numerically equal to the hydrogen-ion concentration which it is desired that the solution shall have. If a weak base is employed instead of a weak acid, the corresponding condition is evidently

$$[OH^-] = K_B \tag{80}$$

Problem 17.—It is desired to prepare a solution having the hydrogen-ion concentration $[H^+]$. The best weak acid which is available happens to be one whose ionization constant is $n[H^+]$. Show that the ratio of salt to acid in the solution should be

$$\frac{C_S}{C_A} = \frac{n}{\alpha_S} \tag{81}$$

Problem 18.—Give complete directions for preparing a *neutral* solution, which possesses equal reserve acidity and reserve alkalinity, by means of a mixture of the two salts NaH_2PO_4 and Na_2HPO_4. With regard to the ionization of its first hydrogen, phosphoric acid is a strong acid. The other two hydrogens ionize in accordance with the equations,

$$\frac{[H^+]\,[HPO_4^{--}]}{[H_2PO_4^-]} = 2.1 \cdot 10^{-7} \tag{82}$$

and

$$\frac{[H^+][PO_4^{---}]}{[HPO_4^{--}]} = 4 \cdot 10^{-13} \tag{83}$$

Problem 19.—The solubility of CO_2 in water at 25° and one atmosphere is 0.0338 formula weight per liter. What will be the true acidity of a 0.12 formal solution of sodium bicarbonate, $NaHCO_3$, which is saturated with CO_2 at 25° and one atmosphere? The ionization constants of carbonic acid at 25° are

$$\frac{[H^+][HCO_3^-]}{[CO_2+H_2CO_3]}=3\cdot10^{-7} \qquad (84)$$

and

$$\frac{[H^+][CO_3^{--}]}{[HCO_3^-]}=6\cdot10^{-11} \qquad (85)$$

Neglect the influence of the salting-out effect.

The actual magnitude of the reserve acidity or reserve alkalinity of a solution depends of course upon the total concentration of the protecting materials. By means of the phosphate mixture mentioned in problem 18, it is possible to prepare a perfectly neutral solution which requires the addition of 0.5 equivalent of HCl per liter before it will show an acid reaction to congo red and which requires the addition of 0.5 equivalent of NaOH per liter before it will exhibit an alkaline reaction toward phenolphthalein. With distilled water, $5\cdot10^{-5}$ equivalents of either reagent would be sufficient to change the color of the indicator. The presence of weak acids and their salts in the saliva, in the blood, and in the other fluids of the animal body is responsible for the power which these fluids possess of protecting themselves against a change in their hydrogen-ion concentration.

8. Neutralization Indicators.—When a solution of a base is titrated with a standard acid, or *vice versa*, the end point of the titration should occur when the amounts of acid and base employed are exactly equivalent to each other. At the end of the titration the composition of the solution should, therefore, be such as would be obtained by dissolving the pure salt in the proper amount of water. Unless the acid and the base are of equal strengths, however, this solution will not be neutral because the salt will be hydrolyzed to some extent. The indicator employed in the titration should not, therefore, in general be one whose color change occurs when the solution is neutral but rather one whose color change takes place when the solution has the particular hydrogen-ion concentration which exists in a pure solution of the salt formed during the titration. Since the standard solution employed in the titration should always be one of a *strong* acid or base (in order that the hydrolysis of the resulting salt shall be as small as possible), it is evident that the choice of a suitable indicator will be determined by the ionization constant of the base or acid which is to be titrated and by the concentration of the salt in the resulting solution.

Indicators are weak organic acids (or bases) whose un-ionized molecules exist in two tautomeric forms[2] in equilibrium with each other in the solution. One of these forms, HIn (or InOH), has the color A and is practically a non-electrolyte. The other form, HIn′ (or InOH′), ionizes, and this form together with the indicator-salt, BIn (or InA), and the indicator-ion, In^- (or In^+), has another color B. For a good indicator either A or B should be white or A and B should be two sharply contrasted colors.

For an indicator-acid the equilibria existing in its solution may be represented thus

$$\underbrace{\mathrm{HIn}}_{\text{color A}} \rightleftarrows \underbrace{\mathrm{HIn}' \rightleftarrows \mathrm{In}^- + \mathrm{H}^+}_{\text{color B}} \tag{86}$$

and for an indicator-base, thus

$$\underbrace{\mathrm{InOH}}_{\text{color A}} \rightleftarrows \underbrace{\mathrm{InOH}' \rightleftarrows \mathrm{In}^+ + \mathrm{OH}^-}_{\text{color B}} \tag{87}$$

For a good indicator the mass action constant

$$\frac{[\mathrm{HIn}']}{[\mathrm{HIn}]} = \text{const. or } \frac{[\mathrm{InOH}']}{[\mathrm{InOH}]} = \text{const.} \tag{88}$$

should be extremely small, that is, the neutral molecules of the

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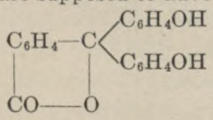
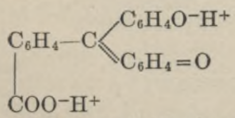
[2] The different colors of the two tautomeric forms are due to different configurations of the molecules. Thus the non-ionizing and ionizing tautomers of phenolphthalein are supposed to have the structures



and



respectively. Phenolphthalein is thus a dibasic acid and in an exact theory of its use as an indicator should be treated as such. [See Rosenstein, Jour. Amer. Chem. Soc., **34**, 1117 (1912).]

ionizing tautomer should be present only to a very slight extent in the solution. Practically all of the indicator should exist either in one or both of the forms HIn and In^-, or InOH and In^+. If this condition is not fulfilled, the color change of the indicator will be gradual instead of sharp.

If we add a strong acid to a solution of an indicator-acid, the above equilibria (equation 86) will all be driven toward the left and the solution will have the color A, the "*acid color* of the indicator," since practically all of the indicator will be present in the form of the molecules HIn. If on the other hand we add a base, BOH, to the solution, the hydrogen-ion concentration will be greatly reduced as a result of the reaction $H^+ + OH^- = H_2O$, and all of the above equilibria will be driven toward the right. The solution will now have the color B, the "*alkaline color* of the indicator," since practically all of the indicator will be present in the form of the salt BIn and its ion In^-. If the hydrogen-ion concentration of the solution is given that particular value which results in half of the indicator being present in the form HIn and the other half in the form $In^- + BIn$, the solution will have the color produced by the mixture of colors A and B in equal proportions. This intermediate color is called the "*neutral color* of the indicator." The solution, however, will not be neutral but will have a value of $[H^+]$ which is determined by the ionization constant of the particular indicator employed. For an indicator-base the behavior is entirely analogous. We shall now proceed to formulate the equilibrium expressions for the ionization of an indicator.

The mass action law gives us for an indicator-acid the expression

$$\frac{[H^+]\,[In^-]}{[HIn]} = K_{IA} \tag{89}$$

and for an indicator-base the expression

$$\frac{[In^+]\,[OH^-]}{[InOH]} = K_{IB} \tag{90}$$

Putting $[OH^-] = \frac{K_w}{[H^+]}$ in equation (90) and solving (89) and (90) for $[H^+]$ we have

$$[H^+] = \frac{K_w}{K_{IB}}\,\frac{[In^+]}{[InOH]} \tag{91}$$

and

$$[\mathrm{H}^+] = K_{IA}\frac{[\mathrm{HIn}]}{[\mathrm{In}^-]} \tag{92}$$

Now [HIn] in the case of an indicator-acid is the concentration of that portion of the indicator which exhibits the "acid color." If $1-\gamma$ is the fractional part of the indicator which exists in this form, then evidently $[\mathrm{HIn}] = (1-\gamma)C_I$ and $[\mathrm{In}^-] = \alpha_{IS}\gamma C_I$, where C_I is the total concentration of the indicator and α_{IS} is the degree of ionization of the indicator-salt. Equation (92) therefore becomes

$$[\mathrm{H}^+] = K_{IA}\frac{1-\gamma}{\gamma\alpha_{IS}} \tag{93}$$

In the case of an indicator-base, if $1-\gamma$ is the fractional part which is present in the form of the salt, that is, in the form which exhibits the "acid color," we have $[\mathrm{In}^+] = \alpha_{IS}(1-\gamma)C_I$ and hence

$$[\mathrm{H}^+] = \frac{K_w}{K_{IB}}\ \frac{\alpha_{IS}(1-\gamma)}{\gamma} \tag{94}$$

Except for the position occupied by the quantity α_{IS} in equations (93) and (94) both equations have the same mathematical form. For most problems involving the use of indicators α_{IS} may be taken as practically equal to unity. If we make this assumption, equations (93) and (94) evidently are identical in form and may be written

$$[\mathrm{H}^+] = K_I\frac{(1-\gamma)}{\gamma} \tag{95}$$

Equation (95) is therefore applicable to any indicator, whether it be an acid or a base. K_I will be called the *indicator-constant.* γ represents the fractional part of the indicator which is present in the form showing the "*alkaline color*" of the indicator. If $\gamma = 0.5$, the indicator will evidently show its "neutral color" and equation (95) yields the important conclusion that the indicator-constant, K_I, of any indicator is equal to the hydrogen-ion concentration of the solution in which that indicator shows its "neutral color." This makes the determination of the indicator-constant of any indicator a comparatively simple matter.

In general, however, it is not the value of K_I alone but rather the value of the "indicator function," $K_I\frac{(1-\gamma)}{\gamma}$, which it is important to know for the different indicators. This is due to the fact that with some indicators the "neutral color" of the indicator is not taken as the end point in a titration, that is, some fraction other than one-half of the indicator is transformed from one form to the other at the end point. The value of this fraction varies with different indicators and is determined by the sensitiveness of the eye to the color changes which occur and by the value demanded for the indicator function in a given titration. Thus, for example, in using phenolphthalein the eye can detect the appearance of the first flush of pink color more accurately than it could determine the exact intensity of red which corresponds to the transformation of one-half of the indicator from the colorless to the colored form. The value of the indicator function for any given value of γ, and hence also the value of the indicator-constant of any indicator, may be determined by observing in a colorimeter the colors displayed by the indicator in a graded series of solutions of known hydrogen-ion concentrations and noting in what solution the indicator displays the desired "*transformation color*." A standard displaying this "transformation color" is prepared by superimposing a tube of a solution showing the "acid color" upon a tube showing the "alkaline color," the depths of the solution in the two tubes being in the ratio $\frac{(1-\gamma)}{\gamma}$.

Table XXIX shows the colors displayed by a number of indicators in solutions of varying hydrogen-ion concentrations. With the aid of this table one can evidently ascertain roughly the values of the indicator-constant for these indicators and with a set of these indicators the approximate value of the true acidity of a given solution could be determined from the above table.

Problem 20.—Which of the indicators in Table XXIX show their "neutral color" in a solution which is actually neutral? A drop of phenolphthalein added to a certain solution gives it a red color, but thymolphthalein is colorless in the same solution. What is the hydrogen-ion concentration of the solution?

Problem 21.—A solution is 0.01 molal with respect to acetic acid and 0.1 molal with respect to sodium acetate. Will the solution react "acid" or "alkaline" to (*a*) methyl orange, (*b*) methyl red, (*c*) litmus, (*d*) phenolphthalein?

Problem 22.—A 0.1*n* solution of methylamine hydrochloride gives a red-violet color with litmus and a yellow color with methyl red. Approximately what is the ionization constant of methyl amine? A more careful

TABLE XXIX.—Color reactions of indicators in solutions of different hydrogen-ion concentrations

	A	1	2	3	4	5	6	7	8	9	10	11	12	13	14
True Acidity = [H⁺]......	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
True Alkalinity = [OH⁻]..	10^{-14}	10^{-13}	10^{-12}	10^{-11}	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
Dimethylamidoazo-benzene	Cherry-red	—+	—+	Flesh-colored	Golden-yellow	+—	+—	+—	+—	+—					
Methyl Orange..........	Rose-red	—+	—+	—+	Orange-red	Yellow	+—	+—	+—	+—					
Sodium-alizarinsulphonate	Greenish Yellow	—+	—+	—+	—+	—+	Red	+—	+—	+—	+—	+—			
Rosolic Acid............			—+	Yellow	—+	—+	—+	Rose	Red	+—	+—	+—			
Guiac Tincture..........				—+	Color-less	—+	—+	—+	Greenish Yellow	+—	+—	+—	+—		
Phenolphthalein.........					—+	Color-less	—+	—+	—+	Red	+—	+—	+—	+—	
Thymolphthalein........							Color-less	—+	—+	—+	Blue	+—	+—	+—	
Tropaolin O............								Yellow	—+	—+	—+	—+	Orange Yellow	+—	+—
Trinitrobenzene.........										Color-less	—+	—+	—+	Orange	+—
Benzopurpurin..........											Yellow	—+	—+	—+	Red
Methyl Red.............			—+	Red	—+	Pink	Yellow	+—	+—						
Congo Red.............			—+	Blue	Violet	Reddish Violet	Orange	Orange-red	+—	+—					
Litmus.................			—+	Red	Red	Red	Red-violet	Violet	Blue	+—	+—				
Cochineal..............			—+	—+	Yellow	Yellow-pink	Lilac	+—	+—						

investigation shows that with paranitrophenol the above solution gives a color which is identical with the color shown by the same indicator when 5 per cent. of it is transformed into its salt. The indicator-constant for paranitrophenol is $9 \cdot 10^{-8}$. Calculate a more exact value for the ionization constant of methyl amine.

In titrating a strong acid or base in a solution containing no other acids or bases the indicator employed should theoretically be one whose indicator function has the value 10^{-7}. Practically, however, almost any sensitive indicator can be employed in such a titration because the addition of the slightest excess of the standard solution produces a large change in the hydrogen-ion concentration of the solution. If the acid or base to be titrated is weak or if the solution contains weak electrolytes in addition to the strong electrolyte to be titrated, then the indicator chosen must be one whose "transformation color" is reached at the proper hydrogen-ion concentration. The following problems illustrate the application of the above principles in choosing indicators. For a more extensive and detailed treatment of the theory of indicators and their application to titrametric analysis the student should consult the paper of A. A. Noyes.[3]

Problem 23.—A certain monobasic acid whose ionization constant is K_A is to be titrated. What should be the value of the indicator function of the indicator employed in the titration, if the concentration of the salt in the solution at the end of the titration is C_S equivalents per liter?

Problem 24.—The ionization constant of butyric acid is $15 \cdot 10^{-5}$. What should be the value of the indicator function of the indicator employed in titrating this acid, if the solution is $0.1n$ at the end of the titration? If the "neutral color" of the indicator is taken as the "transformation color" in the titration, which of the indicators shown in Table XXIX could be employed? Which, if the solution at the end of the titration were only $0.001n$ with respect to the salt?

Problem 25.—A solution contains equivalent amounts of hydrochloric acid and two weak organic acids of ionization constants $3.2 \cdot 10^{-6}$ and $1.8 \cdot 10^{-11}$, respectively. It is desired to determine the concentration of each acid by titrating with standard NaOH solution. If at the end of each titration the volume of the solution is 1 liter, calculate the value which the indicator function should have for each titration. From the indicators shown in Table XXIX select the three which appear to be the most suitable for the purpose. Note that the choice of the indicator for the HCl titration will be determined by the degree of ionization of the first of the two weak acids, the choice of the indicator for titrating the second weak acid will be determined by the degree of hydrolysis of the salt of this acid, while the choice of the indicator for titrating the first weak acid will be determined by a more complicated set of equilibria. Assume that about 0.08 equivalent of NaOH is required to titrate the HCl.

Problem 26.—Calculate the value of the indicator function for each of the three indicators suitable for titrating in succession the three hydrogens of phosphoric acid, assuming that the solution is $0.1n$ with respect to the salt at the end of each titration. (See problem 18, above.)

The accuracy with which the end point of a titration can be determined depends, other things being equal, upon the magnitude of the change in hydrogen-ion concentration produced by the addition of one drop of the standard solution as the end point is approached. This change is smaller, and the titration therefore less accurate, the weaker the acid or base which is being titrated.

Problem 27.—Assuming that at the end of the titration of a strong acid the end point can be detected within one drop (0.03 c.c.) of the $0.1n$ solution of NaOH employed, calculate in drops the sensitiveness of the end point when the acid to be titrated has an ionization constant equal to (*a*) 10^{-4}, (*b*) 10^{-6}, (*c*) 10^{-8}, (*d*) 10^{-10} and (*e*) 10^{-12}. Assume that the solution at the end of the titration has a volume of 1 liter and that it contains 0.1 equivalent of the salt. Assume also that the indicators employed are equally sensitive to a given relative change in the hydrogen-ion concentration of the solution.

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CHAPTER XXIV

THE PHASE RULE

GENERAL

1. Composition-number and Component-number.—Every physico-chemical system (I, 8) is composed of molecules of some kind or kinds and the composition of any phase (I, 8) in such a system may be expressed in terms either of the molecular fractions (II, 6, problem 1) or the per cents. by weight of the different molecular species which compose the phase. Consider any phase which has attained a state of equilibrium with its surroundings at a given temperature T and pressure P. Let the phase be composed of the molecular species S_1, S_2, S_3 . . . S_n. In order that the composition of the phase shall be completely determined it is first necessary that the values of the molecular fractions (or per cents. by weight) of a *certain minimum number* of these molecular species shall be designated. The minimum number (but not the kind) of molecular species whose molecular fractions or per cents. by weight *must* be so designated before the composition of the phase is completely determined will be called the **composition-number, N, of the phase.** If the system under consideration contains more than one phase, then the **composition-number of the system** will be defined as equal to the largest composition-number of any of the phases of the system.

The following examples will help in making clear the significance of the term composition-number:

(*a*) The condition of a phase containing only one species of molecule (pure gaseous argon, for example) is completely determined when its pressure and temperature are given. No specification regarding its composition is required since the per cent. of the given species of molecule can obviously have no value other than 100. The composition-number of any system containing only one species of molecule is therefore *zero.*

(*b*) A liquid consisting of a mixture of two pure substances

(I, 2*b*) contains two molecular species and the molecular fraction or per cent. by weight of at least *one* of these species must be designated before the composition of the phase is determined. Its composition-number is therefore *one*.

(*c*) Liquid water consists (XI, 2) of a number of different molecular species, H_2O, $(H_2O)_2$, $(H_2O)_3$, H^+, and OH^-, all of which are in equilibrium with one another in such a way that, when the temperature and pressure are fixed, the molecular fraction of every species present is also fixed. The composition is thus completely fixed and determined by the temperature and pressure *alone*, no further information being required. The composition-number of the system is therefore *zero*. Note that when we say that the composition of the mixture called water is "completely determined" at a given temperature and pressure, we mean merely that there is only a single composition possible at that temperature and pressure. We do not mean to imply that the composition is actually known.

(*d*) A gaseous phase prepared by bringing together hydrogen, water vapor and oxygen contains the molecular species H_2, O_2, H_2O and doubtless others. At ordinary temperatures in the absence of a catalyst the hydrogen, oxygen and water are not in chemical equilibrium with one another and before the composition of the phase is completely determined it is necessary to state the molecular fraction or per cent. by weight of at least *two* of the molecular species. That is, either the per cent. of water and the per cent. of oxygen, or the per cent. of water and the per cent. of hydrogen, or the per cent. of hydrogen and the per cent. of oxygen must be given before the composition of a phase composed of all three substances is completely determined. The composition-number of the phase is therefore *two*. At sufficiently high temperatures or in the presence of a suitable catalyst, the hydrogen, oxygen and water enter into a chemical reaction and reach a state of equilibrium with respect to this reaction. Under such conditions the composition of the phase will be completely determined, if the molecular fraction or per cent. by weight of a *single* molecular species be designated. The molecular fractions of the other two species are then determined by the fact that they must be such that they will satisfy the equilibrium law expressed by equation (6, XXII) and at the same time fulfill the condition that the sum of the molecular fractions of all the species present must equal unity. The composition-number of the phase is therefore *one.*

We thus see that a system composed of a given number and kind of molecular species may have different composition-numbers according to whether certain chemical equilibria are or are not realized within the system, and since the realization or non-realization of a given chemical equilibrium is frequently dependent upon the time covered by the experiment, a given system might have one composition-number for experiments covering short periods of time and another composition-number for experiments lasting for much longer periods of time. The composition-number of a system is, therefore, not in general a number whose value can be predicted in advance of all experimental investigation of the system. In fact with respect to ultimate and most stable conditions of equilibrium the composition-number of any system would have to be taken as one less than the number of chemical elements in the system. In actual practice, however, the value of the composition-number of a given system is almost invariably obtained by means of the relation, (to be derived below)

$$\text{N} = \text{P} + \text{F} - 3 \tag{1}$$

where F is the number of variants (temperature, pressure and composition-percentages) which the system is found by actual experiment to possess when it contains P phases in equilibrium with one another under a given set of conditions. It is important that these facts with respect to the term composition-number should be clearly appreciated, as failure to do so is one of the common causes of error in applications of the phase rule.

Problem 1.—What is the composition-number of a solution prepared by dissolving in water (*a*) sodium chloride; (*b*) acetic acid; (*c*) potassium nitrate and potassium chloride; (*d*) hydrogen; (*e*) potassium nitrate, sodium nitrate and potassium chloride; (*f*) potassium nitrate, sodium nitrate, potassium chloride and sodium chloride.

In most discussions involving the use of the phase rule it is customary to employ a quantity known as the component-number of the system, in place of the quantity which we have defined above under the name composition-number of the system. By the term **component-number** of (usually called "number of components" of) a system is meant nothing more nor less than simply a number which is greater by one than the composition-number of the system. It is, therefore, evidently quite immaterial which of these numbers one chooses to employ in describing the character of the composition of a system. We shall find it convenient to make use of both numbers in what follows.

2. Derivation of the Phase Rule.—The factors which determine the conditions of equilibrium in any system are entirely independent of the relative or absolute amounts of the different phases present in the system and of the way in which these phases are distributed throughout the system, provided that no phase is present in an exceedingly fine state of subdivision.

Let us consider a system having the composition-number N and the component-number C and containing P phases all in thermodynamic equilibrium with one another. Let the phases be numbered I, II, III . . . P. In any given phase the fugacities (XIV, 1) of *all* the molecular species will be determined as soon as the fugacities of C such species are determined and the fugacities of each of these C species will be determined by the temperature, the pressure and the composition of the phase, or in all by N+2 independent variables. For example, for phase I we would have

$$p_1^{\mathrm{I}} = \mathrm{f}_1^{\mathrm{I}}(P, T, x_1^{\mathrm{I}}, x_2^{\mathrm{I}}, x_3^{\mathrm{I}} \ . \ . \ . \ x_{\mathrm{N}}^{\mathrm{I}}) \qquad (2)$$
$$p_2^{\mathrm{I}} = \mathrm{f}_2^{\mathrm{I}}(P, T, x_1^{\mathrm{I}}, x_2^{\mathrm{I}}, x_3^{\mathrm{I}} \ . \ . \ . \ x_{\mathrm{N}}^{\mathrm{I}}) \qquad (3)$$
$$\vdots$$
$$p_{\mathrm{C}}^{\mathrm{I}} = \mathrm{f}_{\mathrm{C}}^{\mathrm{I}}(P, T, x_1^{\mathrm{I}}, x_2^{\mathrm{I}}, x_3^{\mathrm{I}} \ . \ . \ . \ x_{\mathrm{N}}^{\mathrm{I}}) \qquad (4)$$

and similarly for phase II:

$$p_1^{\mathrm{II}} = \mathrm{f}_1^{\mathrm{II}}(P, T, x_1^{\mathrm{II}}, x_2^{\mathrm{II}}, x_3^{\mathrm{II}} \ . \ . \ . \ x_{\mathrm{N}}^{\mathrm{II}}) \qquad (5)$$
$$p_2^{\mathrm{II}} = \mathrm{f}_2^{\mathrm{II}}(P, T, x_1^{\mathrm{II}}, x_2^{\mathrm{II}}, x_3^{\mathrm{II}} \ . \ . \ . \ x_{\mathrm{N}}^{\mathrm{II}}) \qquad (6)$$
$$\vdots$$
$$p_{\mathrm{C}}^{\mathrm{II}} = \mathrm{f}_{\mathrm{C}}^{\mathrm{II}}(P, T, x_1^{\mathrm{II}}, x_2^{\mathrm{II}}, x_3^{\mathrm{II}} \ . \ . \ . \ x_{\mathrm{N}}^{\mathrm{II}}) \qquad (7)$$

and so on, for each of the other P phases. There are evidently involved in these P sets of equations the two variables P and T, the same for all phases, and N molecular fractions and C fugacities for each phase, or altogether, (PC+PN+2) variables.

Now except in the case of molecular species which resemble each other very closely (such as isotopes (I, 2*c*) or optical isomers (I, 2*d*)), the C equations for any one phase will all be *different* and may, therefore, be treated as C entirely independent equations. We have then PC independent equations. In addition to the relationships expressed by these equations we have the fact that the fugacities of a given molecular species must, at equilibrium, be the same in all the P phases. That is,

$$p_1^{\mathrm{I}} = p_1^{\mathrm{II}} = p_1^{\mathrm{III}} = \ . \ . \ . = p_1^{\mathrm{P}} \tag{8}$$

$$p_2^{\mathrm{I}} = p_2^{\mathrm{II}} = p_2^{\mathrm{III}} = \ . \ . \ . = p_2^{\mathrm{P}} \tag{9}$$

$$\vdots$$

$$p_C^{\mathrm{I}} = p_C^{\mathrm{II}} = p_C^{\mathrm{III}} = \ . \ . \ . = p_C^{\mathrm{P}} \tag{10}$$

This gives us $C(P-1)$ additional equations, or altogether $PC + C(P-1)$ equations connecting the $PC+PN+2$ variables. In order to solve these equations simultaneously it is necessary that the values of F of the variables shall be known, where F is given by the relation

$$\begin{aligned} F &= \text{number of variables} - \text{number of independent equations} \\ &= (PC+PN+2) - (PC + C(P-1)) \\ &= P(N-C) + C + 2 \end{aligned} \tag{11}$$

But by definition (XXIV, 1), $C = N+1$ so that the above relation may be written

$$P + F = N + 3 \tag{12}$$

or

$$P + F = C + 2 \tag{13}$$

In the above derivation we assumed for the sake of generality that each of the C molecular species is present to some extent in every phase of the system. The result would be the same, however, if this condition were not true. Thus, for example, if species 2 were not present in phase I, we should have two less variables (p_2^{I} and x_2^{I}) in our system. But we should have two less equations also (equation (3) and one of the equations (9)), so that the expression for F would be the same as before.

The relationship expressed by equations (12) and (13) is known as the **Phase Rule** and was first deduced by Willard Gibbs.[a] F,

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[a] Josiah Willard Gibbs (1839–1903). Professor of Mathematical Physics at Yale University. One of America's greatest chemists.

the number of variables whose values must be designated before the condition of a system is completely determined, is called the "number of degrees of freedom" possessed by the system.

Problem 2.—What is the maximum number of phases which could exist in equilibrium with one another in a system prepared by bringing together, at ordinary temperatures, water, argon, sodium chloride, silver chloride, and ammonia.

In using the Phase Rule as expressed by equation (12) or (13) the following facts, which were assumed in deriving it, should always be borne in mind.

(1) All phases present in the system must be under the same pressure.

(2) No phase must be present in such a fine state of subdivision that the fugacity of any molecular species contained in it is appreciably influenced by forces of the nature of surface tension.

(3) Aside from composition no variables other than pressure and temperature shall be allowed to influence the system or any of its phases. This excludes such influences as electrostatic or electromagnetic fields, variations in the character or amount of radiant energy which falls on the system, the effect of gravitation, etc. If it is desired to consider the effects of variations in such variables, the Phase Rule can be extended so as to include them, but equation (13) was derived on the assumption that such influences are absent.

(4) The set of fugacity equations (2 to 7) for each phase was assumed to be independent of the fugacity equations of every other phase. If, therefore, in any system two phases should happen to have identical fugacity equations these two phases would be thermodynamically identical and should be classed as a single phase in the sense of the Phase Rule. Thus two crystals which differed from each other only in the respect that one was the mirror image of the other would, if composed of the same species of molecule, be classed as a single phase in the sense of the Phase Rule.

(5) A system composed of isotopes, or in general any system in which the fugacity equation of one of the molecular species in each phase was identical with the fugacity equation of each of the other molecular species in that phase, would, as long as this condition remained true, apparently behave toward pressure and

temperature changes like a system with the component-number one, because instead of having C *independent* fugacity equations for each phase we would have only *one* such equation. Thus, for example, the vapor pressure of a mixture of two optical isomers in the liquid state may be determined solely by the temperature, being independent of the percentage composition of the liquid phase.

According to the number of degrees of freedom which they possess and irrespective of their chemical composition or physical condition, all physico-chemical systems may be classed as either nonvariant, monovariant, divariant, trivariant or tetravariant, etc.

ONE-COMPONENT SYSTEMS

3. The Phase Rule Diagram for a One-component System.—The condition of a system whose composition-number is zero (and whose component-number is therefore *one*) is completely determined by two variables only, the temperature and the pressure, and hence all the relations involved in the Phase Rule for such a system can be displayed graphically on a two-coordinate diagram which is called the *P-T* diagram.

For a one-component system the Phase Rule (equation 12) becomes

$$\mathrm{P}+\mathrm{F}=3 \tag{14}$$

and, if $\mathrm{P}=1$, $\mathrm{F}=2$. That is, before the condition of the system is completely determined *both* its temperature and its pressure must be specified and, within the limits of the existence of the phase, both quantities may be fixed arbitrarily. Such a condition is evidently represented graphically by a surface and any system which possesses two degrees of freedom is said to be **divariant.** All one-component homogeneous systems are, therefore, divariant and will be represented on the diagram by *surfaces.*

If $\mathrm{P}=2$, equation (14) gives $\mathrm{F}=1$. That is, the value of only one of the variables, *either* the temperature *or* the pressure, can be fixed arbitrarily. The value of the other variable is determined by the system itself. A system possessing only one degree of freedom is said to be **monovariant** and is evidently represented graphically by a *curve.* All one-component systems of two phases are, therefore, represented by curves on the *P-T* diagram.

If P = 3, equation (14) gives F = 0. A system possessing no degree of freedom is said to be **nonvariant** and will evidently be represented by a *point.* Every one-component system of three phases will therefore be represented on the *P-T* diagram by a point which is called a **triple point.**

With this general analysis of the way in which phase relations are represented graphically the student should be able to interpret any phase-rule diagram for a one-component system. As an example of such a diagram we shall consider the one representing the system water.

4. The System Water. (*a*) **Water at Low Pressures.**—Fig. 42 shows a portion of the phase-rule diagram for water. In such a diagram the areas representing the divariant systems are named or lettered so as to indicate the particular phase which each area represents. With this information and the scales of pressure and temperature indicated along the axes of the ordinates and abscissæ respectively, the behavior of the system throughout the whole pressure and temperature range covered by the diagram is clearly displayed.

In all the diagrams given in this book the following conventions will be employed. A full heavy line will indicate a stable univariant system which has been studied throughout the range covered by the line. A dotted line will be used to represent a *metastable* univariant system which has been studied throughout the range covered by the line. A light-weight line (whose position is estimated) will be used to represent a univariant system in a region where no actual measurements on the system have been made. By a metastable system is meant one which is in a supercooled or superheated condition (IV, 9).

Problem 3.—What are the possible nonvariant and the possible monovariant systems composed of water in the region covered by Fig. 42? Why is the triple point not located exactly at 0°? (Cf. II, 5, and XXII, 11.)

Problem 4.—Show with the aid of the Second Law of thermodynamics that the portion of the vapor pressure curve of a liquid which lies below the freezing point (*i.e.*, the metastable portion) must always lie above the vapor pressure curve of the crystals. In a similar way it may be shown that the prolongation of *any* curve beyond a triple point must lie *between* the other two curves which meet at that point.

Problem 5.—Take up in succession each one of the numbered dots in Fig. 42. What is the condition of the system at the point represented by the dot? If the heat content of the system be (1) increased continuously and (2) decreased continuously at constant pressure, describe (as far as possible from the diagram) the phase changes which will take place within the system, stating the temperature at which each change occurs. Give a similar description of the phase changes which will occur if the pressure on the system be continuously (1) lowered and (2) raised at constant temperature. Assume that the system remains in a condition of stable equilibrium throughout.

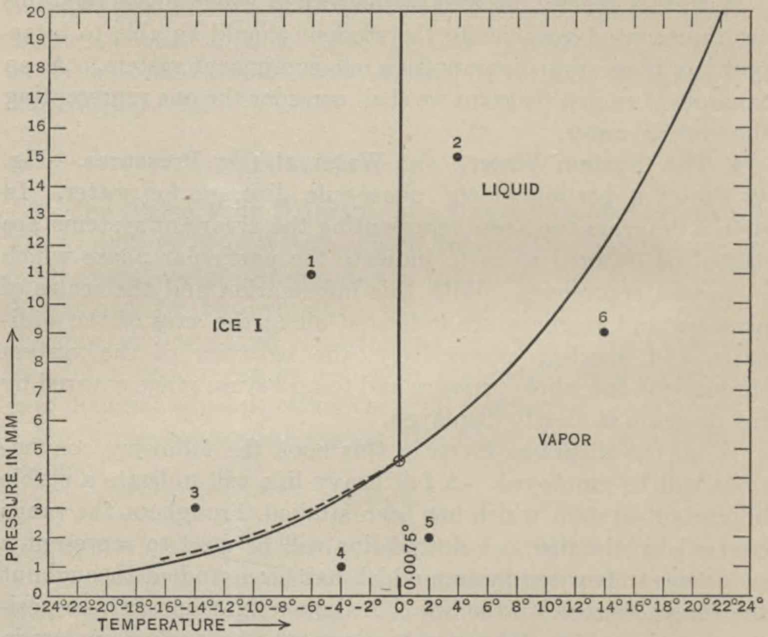
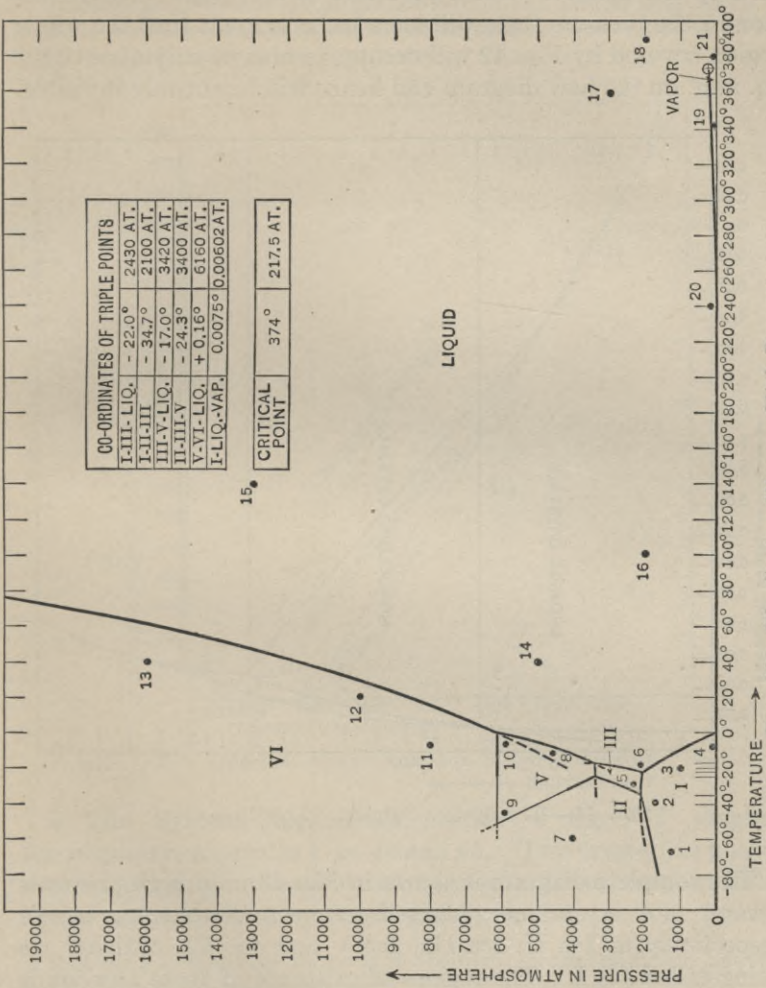


FIG. 42.—The System Water. Low Pressures.

(*b*) **Water at High Pressures.**—Fig. 42 covers a comparatively small range of temperature and pressure. At higher temperatures we know that the vapor pressure curve of liquid water keeps on rising until it comes to an end at the critical point (IV, 7) and the vapor pressure curve for ice probably decreases continuously and becomes zero at the absolute zero.

The course of the ice-liquid curve, however, which seems to rise vertically with increasing pressure, offers some interesting possibilities. Does it continue to rise indefinitely or do new phases eventually appear? This interesting question has been answered by the recent researches of Tammann[a] and of Bridg-



CO-ORDINATES OF TRIPLE POINTS		
I-III-LIQ.	- 22.0°	2430 AT.
I-II-III	- 34.7°	2100 AT.
III-V-LIQ.	- 17.0°	3420 AT.
II-III-V	- 24.3°	3400 AT.
V-VI-LIQ.	+ 0.16°	6160 AT.
I-LIQ.-VAP.	0.0075°	0.00602 AT.
CRITICAL POINT	374°	217.5 AT.

Fig. 43.—The System Water. High Pressures.

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[a] Gustav Tammann (1861–). Professor of Inorganic Chemistry at the University of Göttingen, Germany.

man,[a] who have studied this system up to many thousand atmospheres. In order to display their results graphically we shall have to reduce greatly the scale of the ordinates, in order to keep the diagram within the space of one page. The reduction in the pressure scale will have to be so great that the whole region covered by Fig. 42 will occupy an area of only about 10^{-8} sq. mm. on the new diagram and hence will be entirely invisible.

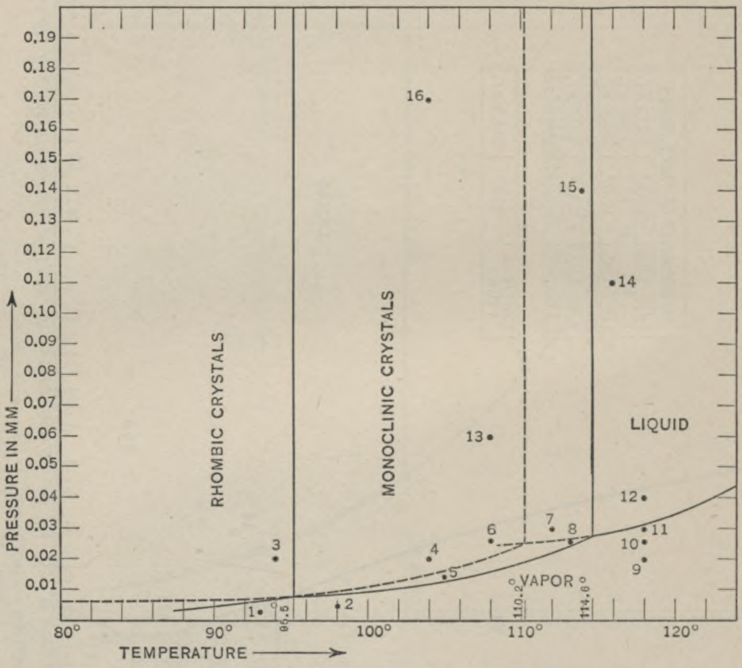

Fig. 44.—The System Sulphur. Low Pressures.

The complete diagram is shown in Fig. 43. At high pressures several new crystalline phases have been discovered, known respectively as Ice II, Ice III, Ice V and Ice VI, ordinary ice being called Ice I. The regions of existence of these new kinds of ice are indicated on the diagram. Note that ice II has no melting point but has three transition points. The melting-point

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[a] Percy Williams Bridgman (1882–). Research Fellow in Physics at Harvard University.

curve of ice VI slopes to the *right*. This is the normal behavior of the melting-point curves of most substances.

Problem 6.—Solve problem 5, using Fig. 43.

Problem 7.—With the aid of the theorem of LeChatelier state as far as possible from the diagram in Fig. 43 which of the various forms of ice are lighter and which are denser than water.

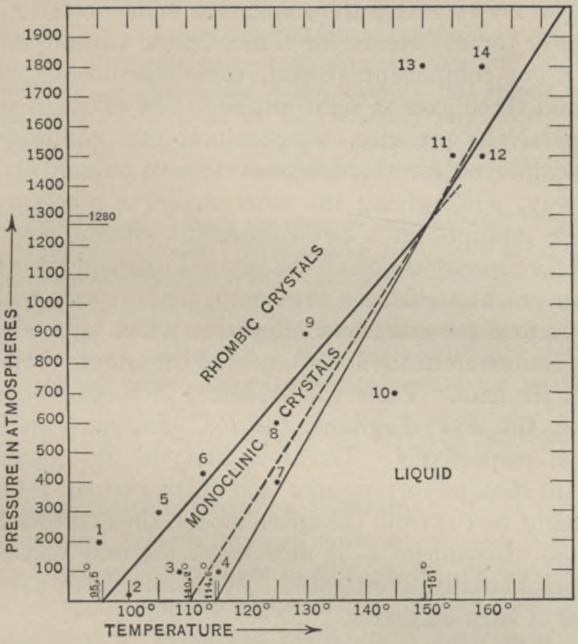

FIG. 45.—The System Sulphur. High Pressures.

5. The System Sulphur.—A portion of the *P-T* diagram for sulphur is shown in Figs. 44 and 45. Two crystalline phases, monoclinic sulphur and orthorhombic sulphur, are included in the region covered by the diagrams.

Problem 8.—What are the possible divariant, monovariant and nonvariant systems in the case of sulphur?

Problem 9.—Solve problem 5, using Figs. 44 and 45. Consider also the cases which might arise if the system passed into the metastable regions.

Problem 10.—Which has the greater density, (*a*) monoclinic sulphur or orthorhombic sulphur; (*b*) monoclinic sulphur or the liquid; (*c*) orthorhombic sulphur or the liquid?

Problem 11.—Show how one may determine, by purely thermodynamic reasoning, which of the two crystalline forms of sulphur is the more soluble in carbon bisulphide at room temperature. How could the transition temperature be determined from solubility measurements?

TWO-COMPONENT SYSTEMS

6. Space Models.—For a two-component system the Phase Rule gives $F=4-P$ and the maximum value which F can have is evidently three. Hence for the complete graphic representation of a two-component system, three coordinates will be required and three axes at right angles to one another, representing respectively pressure, temperature, and composition, are usually employed for this purpose. Space models constructed in this way, while giving the most complete representation of the phase relations in a two-component system, are not well adapted for representation on the printed page, and it is therefore more convenient to discuss two-component systems with the aid of the various *two-coordinate* diagrams which are obtained by cutting sections from the space model of the system perpendicular to one of the axes. There will evidently be three groups of such diagrams, the *P-T* diagrams, the *P-C* diagrams, and the *T-C* diagrams, respectively. The *P-T* and the *T-C* diagrams are usually the most important ones, and of the various *T-C* sections which might be cut from the space model, the one corresponding to $P=$ one atmosphere is in most cases the only one which has been experimentally investigated. We shall take up a few typical examples of such diagrams.

7. Vapor Pressures of Salt Hydrates.—A considerable number of different crystalline phases are frequently formed in a system composed of water and a salt. Thus, for example, stable crystals having the following compositions can be obtained, under suitable conditions, from a system composed of water and ferric chloride: H_2O, $FeCl_3$, $FeCl_3 \cdot 2H_2O$, $FeCl_3 \cdot 2\frac{1}{2}H_2O$, $FeCl_2 \cdot 3\frac{1}{2}H_2O$, and $FeCl_3 \cdot 6H_2O$. Let us consider first the *P-T* diagrams of the different crystal-vapor systems which can be formed from the above phases. With the aid of the Phase Rule and the principle governing chemical equilibrium in heterogeneous systems (XXII, 8), the behavior of two-component crystal-vapor systems under equilibrium conditions can be easily predicted, as will be seen from the solution of the following problems.

Problem 12.—If the presence of the liquid phase be excluded, what are the possible divariant and the possible monovariant systems which can be prepared from water and ferric chloride?

Problem 13.—Is it possible for crystals of $FeCl_3 \cdot 3\frac{1}{2}H_2O$ to exist in equilibrium with water vapor at more than one pressure at a given temperature?

Problem 14.—A mass of crystals having the composition $FeCl_3 \cdot 6H_2O$ is placed in a cylinder provided with a frictionless piston, and the initial pressure upon the piston is made so great that there is no vapor phase in the cylinder. Suppose now that the pressure on the piston be very gradually reduced to zero, the temperature remaining constant. If values of the pressure and corresponding values of the volume of the system be plotted on cross-section paper as ordinates and abscissæ respectively, what will be the general character of the diagram obtained? Assume that conditions of stable equilibrium are maintained in the system throughout the experiment.

Problem 15.—Crystals having the composition $CaCl_2 \cdot 6H_2O$ are obtained by cooling an aqueous solution. After drying the crystals as far as possible with the aid of a centrifuge, it is desired to remove the last remaining traces of adherent water by passing a current of air through and over the mass of crystals spread out in a long tube. What condition must be fulfilled in order that the dried crystals shall have the composition $CaCl_2 \cdot 6H_2O$? What would be the easiest and most certain method for producing this condition?

Problem 16.—Under what condition will a crystal (*a*) deliquesce; (*b*) effloresce, when exposed to the air?

8. Temperature-Concentration Diagrams.—If the pressure on a two-component system be kept constant at such a value that the vapor phase never appears in the system, we have only two variables at our disposal, temperature and composition. The composition may be expressed as the mole fraction or per cent. by weight of any molecular species present in the system, or it may also be expressed in terms of the per cent. by weight of any one of the *chemical substances* from which we choose to consider the system to be prepared, the term *chemical substance*, in this connection, being understood to mean any material which behaves like a one-component system. A temperature-composition diagram of this kind is much used in the phase-rule treatment of metallurgical systems and has many advantages.

Instead of making the composition of the *whole system* one of our variables in the diagram we may take in its place the composition of one of the phases. This is a common practice in the case of solutions in equilibrium with crystalline phases. Such a diagram is called a freezing-point-solubility diagram and the nature of the diagram for a very simple system has already been discussed (XIV, 12, Figs. 23 and 24). We shall now proceed to a consideration of the more complicated freezing-point-solubility diagram which is obtained when the two constituents from which the system is prepared form a series of crystalline compounds with each other.

Examples of such diagrams for systems composed of a salt and water are shown in Figs. 46 to 48. In these figures the ordinates represent temperature and the abscissæ per cent. by weight of the salt in the solution. Any point in the area above and to the left of the set of curves represents a one-phase system, namely, a solution having the composition and temperature indicated by the coordinates of the point. Since we have agreed to keep the pressure constant, a solution represents a divariant system. Any point on one of the curves represents a monovariant system, a

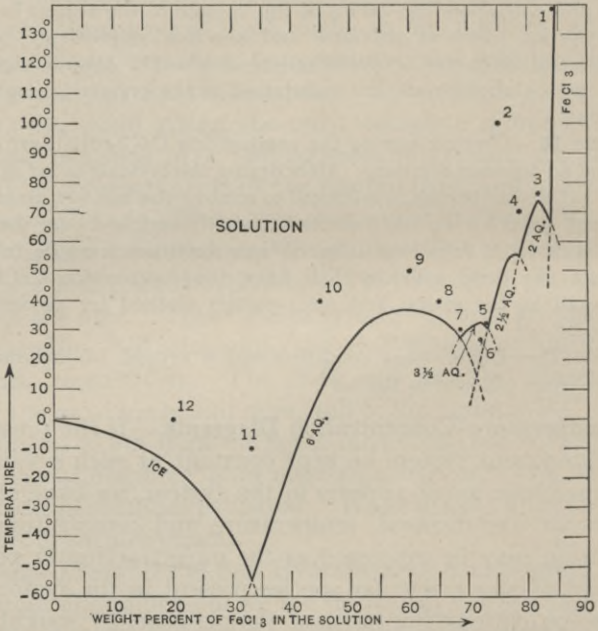

Fig. 46.—The Freezing-Point-Solubility Diagram for Aqueous Solutions of Ferric Chloride.

solution (of the composition given by the abscissa of the point) in equilibrium with a crystalline phase of the nature indicated by the label on the curve. Points in the region below and to the right of the set of curves have obviously no meaning as far as stable systems are concerned, but for metastable systems (*i.e.*, supercooled solutions) they would have the same significance as points above the curves. The conventions with regard to the use of full and of dotted lines, etc., described above (XXIV, 4*a*), apply also to these figures. We shall now proceed to consider in detail some of the principal features of these diagrams.

9. Eutectic Points and Melting Points of Compounds.—Suppose we start with pure water in equilibrium with a large excess of ice, and gradually add crystals of $FeCl_3$ to the system. These will dissolve in the liquid water and the freezing point of the solution formed will fall gradually and continuously as shown by the ice curve in Fig. 46. When a temperature of $-55°$ is reached the further addition of $FeCl_3$ to the system will not cause a further lowering of the temperature, but instead a second crystalline phase, having the composition $FeCl_3{\cdot}6H_2O$, will make its appearance, and since we now have *three* phases the system becomes nonvariant. This temperature, at which the ice and the crystalline hydrate, $FeCl_3{\cdot}6H_2O$, are both in equilibrium with the solution, is evidently a *eutectic temperature* (XIV, 12). After the appearance of this crystalline hydrate, if heat be abstracted from the system, the whole solution will solidify at constant temperature into a mechanical mixture of ice crystals and hydrate crystals in the proportions indicated by the abscissa of the eutectic point.

Starting now at the eutectic point and having present a large excess of the hydrate crystals let us add heat to the system. The ice will gradually disappear and finally we shall be left with a two-phase system consisting of the solution and the hydrate crystals. If we continue to add heat, the temperature of the system will rise and more and more ferric chloride will pass into solution. The variation of composition with temperature is indicated by the curve labeled 6*aq* in the figure. This is the solubility curve for the hydrate, $FeCl_3{\cdot}6H_2O$. Eventually the solution will attain the composition 60 per cent. $FeCl_3$ and 40 per cent. water. As indicated by the figure, a solution of this composition is in equilibrium with crystals of the hydrate at a temperature of 37°, which is the highest point on the solubility curve. The composition of the hydrate crystals is also 60 per cent. $FeCl_3$ and 40 per cent. water, so that this temperature is the melting point of these crystals. If to a system composed of crystals of $FeCl_3 \cdot 6H_2O$ and their melt we add either $FeCl_3$ or H_2O, we should lower the freezing point (Cf. XI, 8) of the liquid. This is shown in the figure by the falling away of the curve on both sides of the temperature 37°. The addition of water would cause the freezing point to fall until the eutectic point $-55°$ was reached once more. The addition of $FeCl_3$, however, would cause the freezing point to fall until the temperature 27.4° was reached. Here a second crystalline hydrate having the composition $FeCl_3 \cdot 3\frac{1}{2}H_2O$ makes its appearance, and our system again becomes nonvariant at this new eutectic point.

The rest of the diagram will now be easily understood. There are evidently five stable eutectic points at the temperatures $-55°$, 27.4°, 30.0°, 55.0°, and 66.0° respectively. One metastable eutectic point at the temperature 15° has also been realized experimentally. There are also four melting points of pure compounds shown, namely, $FeCl_3 \cdot 6H_2O$ at 37.0°, $FeCl_3 \cdot 3\frac{1}{2}H_2O$ at 32.5°, $FeCl_3 \cdot 2\frac{1}{2}H_2O$ at 56°, and $FeCl_3 \cdot 2H_2O$ at 73.5°. The shape of the solubility curve in the neighborhood of the melting point of a compound indicates in a general way the extent to which the compound is broken up into its constituents in the melt. A curve with a very flat peak shows a high degree of dissociation in the melt, while a sharp peak shows that the crystals of the compound melt practically without decomposition.

10. Transition Points.—The freezing-point-solubility diagram for the system water-zinc-chloride is shown in Fig. 47. The solubility curves for four crystalline hydrates appear on the diagram. Let us consider first the solubility curve for the hydrate $ZnCl_2 \cdot 4H_2O$. Starting at the eutectic point, $-62°$, and gradually raising the temperature, the amount of zinc chloride in the solution increases as shown by the curve, and at a temperature of about $-29.4°$ the composition of the solution would become the same as that of the crystals and this temperature would therefore be the melting point of the hydrate. Before this temperature is reached, however, a new crystalline hydrate,

$ZnCl_2 \cdot 3H_2O$, makes its appearance in the system, and since we now have three phases the system becomes nonvariant. The temperature, −30°, at which this occurs is called a **transition point.** If we should continue to add heat to the system at this point, the reaction

$$ZnCl_2 \cdot 4H_2O = ZnCl_2 \cdot 3H_2O + H_2O \qquad (15)$$

would take place and the temperature would remain perfectly constant until all of the higher hydrate had decomposed, and we should be left with the monovariant system made up of the solution and crystals of the hydrate, $FeCl_3 \cdot 3H_2O$. If the lower hydrate should fail to appear when the temperature −30° was reached, we might succeed in carrying the system up to the melting point of the higher hydrate, but the system would then evidently be in a metastable condition. Of the remaining hydrates shown in this diagram, evidently only the one having

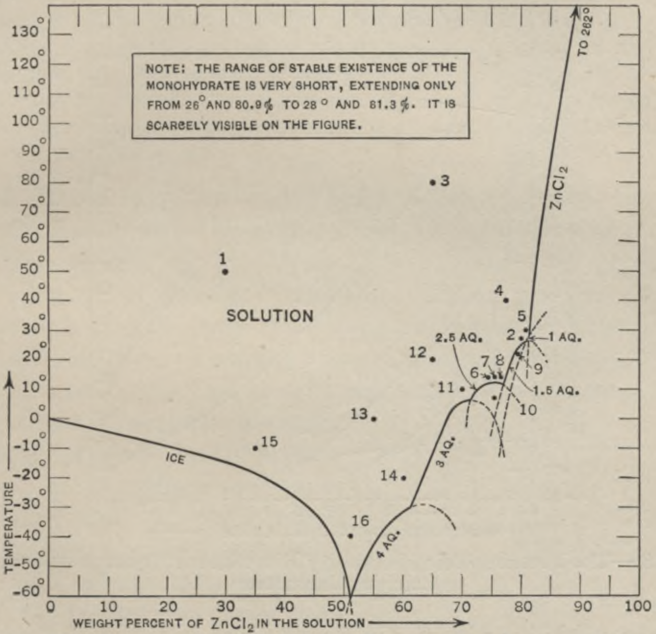

FIG. 47.—The Freezing-Point-Solubility Diagram for Aqueous Solutions of Zinc Chloride.

the formula $ZnCl_2 \cdot 2\frac{1}{2}H_2O$ has a stable melting point. In the case of the others a transition point intervenes in each instance before the melting point is reached. The figure shows the existence of two stable and several metastable eutectic points, and four stable and one metastable transition point.

Problem 17.—How would you prepare crystals of $ZnCl_2 \cdot H_2O$?

11. Retrograde Solubility Curves and Metastable Compounds.—In Figs. 46 and 47 the solubility curves all indicate an *increase* in solubility with rise in temperature and each of the compounds shown has a certain definite range of stable existence, although the range of existence of the hydrate, $ZnCl_2 \cdot H_2O$, is very short. In Fig. 48 is shown an interesting system in which there are four crystalline hydrates, no one of which has *any* range of stable existence (at any rate under atmospheric pressure), the solubility curves being located entirely within the metastable region. Moreover, it will be noticed that the solubility of the anhydrous salt *decreases* rapidly with rising temperature. This is also true of the solubilities of three of the

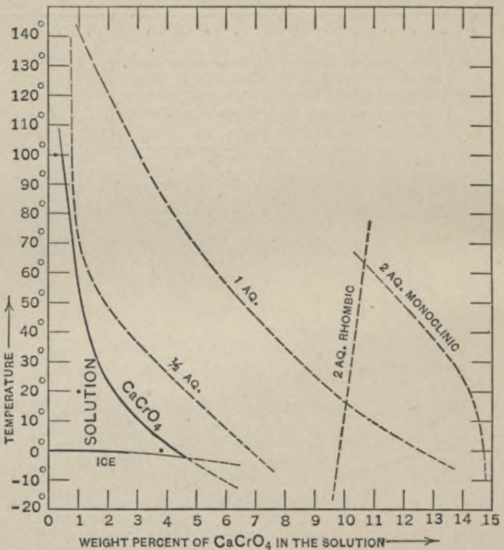

FIG. 48.—The Freezing-Point-Solubility Diagram for Aqueous Solutions of Calcium Chromate.

hydrates. No transition points, no melting points of compounds, and no eutectic points have been actually observed with this system, although the approximate positions of several such points can be inferred from the directions of the curves.

Problem 18.—With the aid of Fig. 47 describe the character and range of existence of each of the (*a*) nonvariant, (*b*) monovariant and (*c*) divariant stable and metastable systems which can be produced from $ZnCl_2$ and H_2O.

Problem 19.—Describe the character and condition of each of the *solutions* represented by the numbered dots in Fig. 47. Describe in each instance the changes which may take place (1) if heat be continuously abstracted from the system and (2) if a current of dry air be passed continuously through the thoroughly stirred system at constant temperature.

Problem 20.—The same as problems 18 and 19, using Fig. 48.

Problem 21.—Explain the action of a mixture of ice and common salt as a **freezing mixture.** What determines the lowest temperature attainable with a freezing mixture?

12. Mixed Crystals and "Solid Solutions."—In the temperature-composition diagrams shown in Figs. 46 to 48 the composition of *only the liquid phase* was subject to continuous variation. The different crystalline phases all had constant compositions. In some two-component systems, however, the crystals deposited on cooling a solution contain both constituents in continuously varying proportions, that is, the two constituents of the system are miscible in the crystalline state in all proportions. A two-phase system of this character consists therefore of *two* solutions, one liquid solution and one crystalline solution (XI, 3*b*) (called also "solid solution"), in equilibrium with each other; and the temperature-concentration diagram for the system must obviously contain *two* curves, one curve to represent the compositions of the liquid solutions and another curve to represent the compositions of the crystalline solutions which at the various temperatures are in equilibrium with each other.

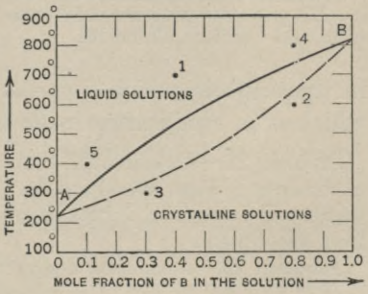

Fig. 49.

Diagrams of this character are shown in Figs. 49 to 51. The full line is the curve for the liquid solution and the long-dash line the curve for the crystalline solution. Evidently the field above the curves represents liquid solutions and the field below the curves, crystalline solutions. The field between the curves has no meaning as far as stable systems are concerned, but any point in this field might of course represent a supercooled liquid solution. It has not been found possible to *superheat* crystals.

The upper curve may be called the *crystallization-point curve* and the lower curve the *melting-point curve* for the system. It is evident from Figs. 49, 50 and 51 that the crystallization temperature of a liquid is sometimes raised and sometimes lowered by dissolving something in the liquid. (Cf. XII, 6.) As a general rule, the crystallization temperature is raised when the mole fraction of the "dissolved substance" is greater in the crystals which separate than it is in the liquid solution which is in equilibrium with them, and *vice versa*.

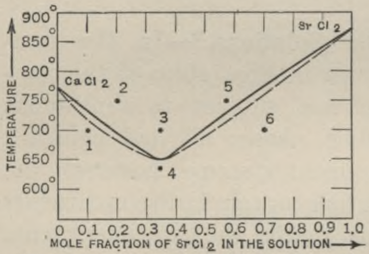

Fig. 50.—Freezing-Point-Solubility Diagram for Mixtures of Strontium and Calcium Chlorides.

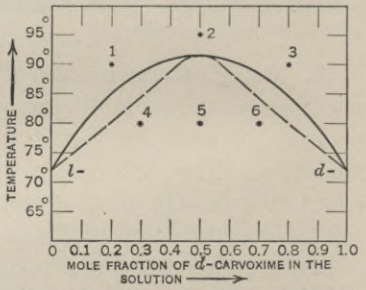

Fig. 51.—Freezing-Point-Solubility Diagram for Mixtures of *d*- and *l*-Carvoxime.

Problem 22.—Describe the character of the system represented by each of the dots in Figs. 49, 50 and 51. Describe fully in each case the changes which will take place, if heat be gradually (1) added to and (2) abstracted from the system.

Problem 23.—A solution represented by each of the dots in the upper part of Figs. 49, 50 and 51 is subjected to fractional crystallization. What will be the character of the two fractions finally obtained in each instance? (See XIV, 19.)

13. Systems Containing Two Liquid Phases of Variable Composition.—Evidently whenever a two-component system contains two non-miscible solutions, whatever be the state of aggregation of these solutions, the temperature-composition diagram for the system must contain two curves in order that the variation of the composition of both solutions with the temperature may be displayed. Systems in which one of the solutions is liquid and the other crystalline have just been discussed. Examples of similar diagrams for systems in which two liquid solutions appear are shown in Figs. 52 and 53.

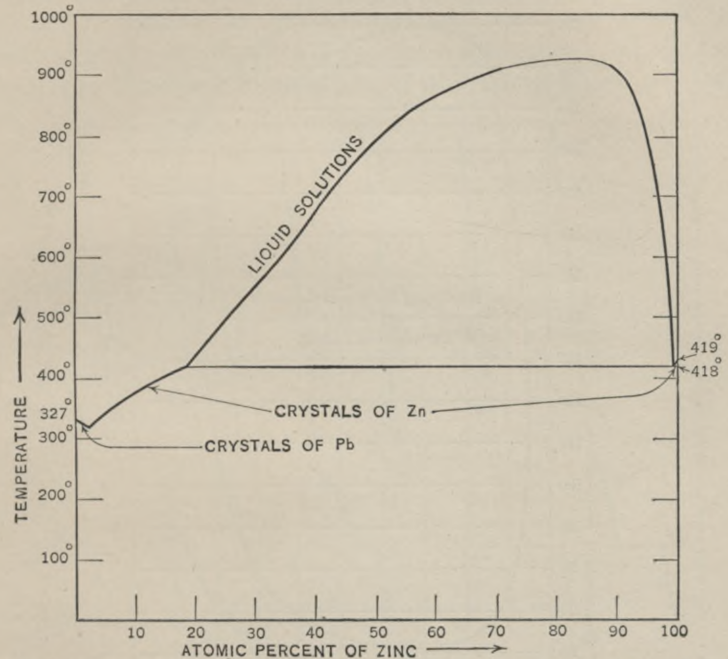

Fig. 52.—Temperature-Composition Diagram for the System Zinc-Lead.

Problem 24.—Interpret the diagrams shown in Figs. 52 and 53.

Problem 25.—Metallic silver and gold are much more soluble in molten zinc than in molten lead. With the aid of the facts displayed in Fig. 52, outline a method for extracting these metals from lead bullion containing only small quantities of the two metals.

14. The Preparation of a Temperature-Composition Diagram. Cooling Curves.—In order to construct the temperature-composition diagram for a given two-component system at constant pressure it is necessary to determine, at a sufficient number of different temperatures, the compositions of both phases in all of the two-phase systems formed. The most accurate method of accomplishing this is by chemical analysis of the two phases which have been brought into equilibrium with each other at each of the measured temperatures. If the temperatures are very high, however, this method frequently becomes very difficult to carry out and in any event may be rather long. A quicker method, applicable to any temperature range and sufficiently exact for many purposes, is used extensively in the study of alloys. This method, known as the method of "thermal analysis," is based upon the character of the cooling curves obtained with liquid mixtures of varying compositions. If we start with

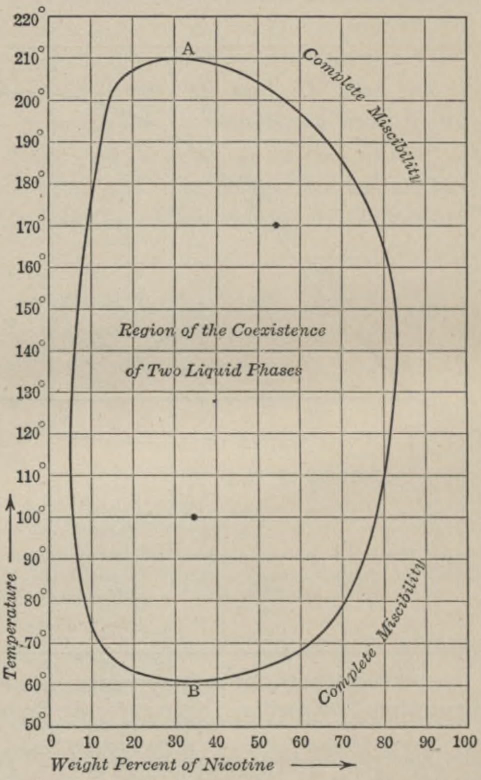

FIG. 53.—A Portion of the Phase Rule Diagram for the System Nicotine-water. [Hudson, Z. phys. Chem. 47, 114 (1903).]

a two-component liquid system and allow it to cool slowly, preferably with constant stirring, the curve obtained by plotting temperature against time is called the *cooling curve* of the mixture. As long as the system contains only the one liquid phase the cooling curve will be a smooth, continuous curve. If a second phase of different composition than the liquid phase appears, the cooling curve will show a sudden change in direction (a "break"), because as the temperature continues to fall the composition of the liquid will change continuously. If the new phase has the same composition as the liquid phase the temperature will remain perfectly constant (a "halting point") for a period, while the liquid phase is completely transformed into the new phase. If at any temperature three phases coexist, the system becomes nonvariant and a halting point will also be obtained and will continue until one of the phases disappears.

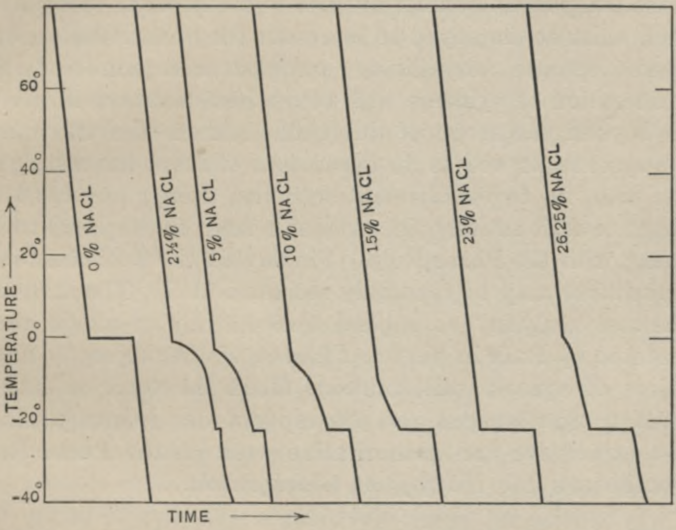

FIG. 54.—Cooling Curves for Aqueous Solutions of Sodium Chloride.

In constructing temperature-composition diagrams from cooling curves it is customary to take the composition of the whole system as one of the coordinates instead of merely the composition of one of the phases of the system. In such a diagram every point on the plane will have a definite significance, since it will represent a system of definite composition in a definite state or states of aggregation. In the following problem the composition of the whole system should be taken as the abscissa.

Problem 26.—Construct the temperature-composition diagram for the system NaCl-H_2O, using the set of cooling curves shown in Fig. 54.

POLY-COMPONENT SYSTEMS

15. Complex Diagrams.—The complete phase-rule diagram for a system requires for its representation $c+1$ coordinates. As the component-number of the system increases, the diagrams which must be employed to represent the phase relations in the system become exceedingly complex and numerous. The consideration of systems with component-numbers larger than 2 is beyond the scope of this book, and for the treatment of such systems as well as for discussions of many interesting cases met with in two-component systems, which we have been obliged to omit entirely, the student is referred to special treatises dealing with the Phase Rule. Findlay's *The Phase Rule and Its Applications* may be especially recommended. The methods of "thermal analysis" as applied to the study of alloys are well presented by Ruer in his *The Elements of Metallography*, and the subject of aqueous salt solutions forms the topic of Jänecke's *Gesättigte Salzlösungen vom Standpunkt der Phasenlehre.* The most exhaustive and authoritative work on the Phase Rule is Roozeboom's *Die Heterogenen Gleichgewicht.*

CHAPTER XXV

DISPERSE SYSTEMS

GENERAL CHARACTERISTICS AND CLASSIFICATION OF DISPERSE SYSTEMS

1. Disperse Systems and the Phase Rule.—If we imagine any phase within a given system to be gradually broken up into smaller and smaller particles, then as the size of these particles gradually decreases the surface of contact between this phase and its neighbors will correspondingly increase and the effects of forces of the nature of surface tension (III, 3) will gradually become more apparent, and these surface forces will eventually begin to be an important factor in determining the fugacities of the molecular species composing the system. Whenever this situation exists to an appreciable extent in any instance, we have what is called a **disperse system** or a **dispersoid,** and the Phase Rule in the form derived and discussed in the preceding chapter is no longer applicable to the system. (See XXIV, 2.) The influence of these surface forces is usually entirely inappreciable, however, unless the particles of the dispersed phase are of microscopic or submicroscopic dimensions, or unless the dispersed phase constitutes a relatively large proportion of the system.

The varied and peculiar properties and behavior displayed by disperse systems, which distinguish these important systems from the ordinary non-dispersed or **aggregated systems,** are due to the relatively enormous surface possessed by the dispersed phase. The **degree of dispersion** of a dispersed phase is usually defined as the ratio of its surface to its volume, or in other words, it is the surface exposed by 1 c.c. of the dispersed material.

Problem 1.—What is the degree of dispersion of gold in a colloidal solution of the metal made up of spherical particles 3 $\mu\mu$ in diameter? What is the degree of dispersion of 1 gram of gold in the form of a sphere? Compare the two. (See problem 2, IX.)

The "*colloidal solutions*" described in Chapter IX are examples of disperse systems. Certain kinds of true solutions (that is, *molecularly dispersed solutions,* Cf. XI, 1) in which one of the constituents is a substance of very high molecular weight (Cf. problem 9, XIV) frequently display many of the characteristics of disperse heterogeneous systems and are for this reason usually classified with them for purposes of systematic treatment.

2. One-component Disperse Systems.—A system composed of a fine mist of liquid water suspended in water vapor is an example of a one-component disperse system. Such a system is a divariant instead of a monovariant one, however (Cf. problem 3, XXIV), because the vapor pressure of a liquid in the form of small droplets is not determined by the temperature alone, but depends also upon the diameter of the drops. The smaller the drops, the higher will be their vapor pressure. A pure liquid in the form of a fine mist or cloud is therefore a metastable (XXIV, 4) system since the small drops have a higher vapor pressure than the larger ones, and hence the latter tend to grow gradually at the expense of the former, until they attain such a size that the influence of surface tension upon vapor pressure becomes inappreciable.

If the individual drops in a fine mist are charged with an electric charge, as would be the case if they were produced by condensation in an ionized gas (I, 2*g*), the presence of the charge will lower the vapor pressure of the drop, and since also the coalescence of the drops by mutual collisions is hindered by the electrical repulsion existing between them, such a mist may persist for a considerable length of time. The presence of electrical charges on colloidal particles is a common phenomenon which is largely responsible for the comparative stability of many disperse systems.

Not only is the vapor pressure of a substance in the dispersed condition different from its vapor pressure in the form of large aggregates, but its melting point, its chemical activity and many other properties are also different. The difference is of course only one of degree, however, not one of kind, the variation in the magnitude of any given property with increasing degree of dispersion being a perfectly gradual one. The curve showing the relation between any given property and the degree of dispersion will have the same general form as the one mentioned in the following problem.

Problem 2.—With the aid of the Second Law of thermodynamics the following expression for the rate of change of the vapor pressure (p) of a drop of liquid with the radius (r) of the drop can be derived:

$$\left(\frac{\partial p}{\partial r}\right)_T = \frac{-2\gamma V_o}{(v_o - V_o)r^2} \tag{1}$$

where γ is the surface tension of the liquid, V_o its molal volume and v_o the molal volume of the vapor. Show that if the vapor is a perfect gas and γ is a constant, the integral of this equation is practically

$$RT \log_e \frac{p}{p_A} = \frac{2\gamma V_o}{r} \tag{2}$$

where p_A is the vapor pressure of the liquid in the aggregated or non-dispersed condition (*i.e.*, where $r = \infty$). Calculate the vapor pressure of water at 0° in the form of small drops when the radius of the drops is (*a*) 10^{-1}, (*b*) 10^{-2}, (*c*) 10^{-3}, (*d*) 10^{-4}, (*e*) 10^{-5} and (*f*) 10^{-6} mm. respectively. (See problem 1, III, and Fig. 43 for additional data.) Construct a curve on cross-section paper showing the relation between the vapor pressure of water and its degree of dispersion. What effect will a variation of the constant γ have upon the curve?

3. Classification of Disperse Systems with Reference to the Nature of the Contact Surface.—Disperse systems may be grouped into the following four classes and subclasses in accordance with the nature of the phases in contact:

I. Contact surface, gas-liquid. (*a*) A liquid dispersed in a gas. Examples: mist, fog, clouds, and spray. (*b*) A gas dispersed in a liquid. Examples: foam, suds, and lather.

II. Contact surface, gas-crystal. (*a*) Crystals dispersed in a gas. Examples: smoke, dust, and fumes of various kinds. (*b*) A gas dispersed in a crystal. Example: certain solid foams.

III. Contact surface, liquid-liquid. Examples: emulsions of one liquid in another. Milk is an emulsion of fats in water.

IV. Contact surface, crystal-liquid. Crystals dispersed in a liquid. A large number of the colloidal solutions and suspensions familiar to the chemist are of this character.

The last two classes of disperse systems are the most important ones and have received the greatest amount of attention from investigators. The discussion of disperse systems in the following pages will be restricted almost entirely to these two classes of systems.

4. The Phenomenon of Adsorption.—When any solid material is brought into contact with a gas or a liquid, the surface layer of the solid dissolves or **adsorbs** some of each of the constituents of the gas or liquid with which it is brought into contact. The amount of adsorption in any given case is directly proportional to the area of the contact surface, but the proportionality constant is a specific constant characteristic of the chemical nature and physical condition of the two phases in contact. Evidently a highly dispersed material may exhibit a very large adsorbing power owing to the enormous surface exposed.

A common example of adsorption is the behavior of finely divided porous charcoal in taking up large quantities of gases. This property is sometimes made use of in producing high vacua. For this purpose a bulb containing cocoanut charcoal is sealed to the vessel which it is desired to exhaust. The bulb is first heated to expel the gases already adsorbed in the pores of the charcoal and then, after closing the vessel and allowing the tube containing the charcoal to cool, a tube containing liquid air is brought up around the bulb of charcoal which will then adsorb practically all of the gas contained in the vessel. A vacuum as high as 0.001 mm. of Hg may be conveniently obtained in this way without the aid of any pump. The use of powdered or animal charcoal in decolorizing solutions is another instance of its high adsorptive power.

Whenever a precipitate is produced in a solution it always carries down with it by adsorption some of the constituents of the solution, and in nearly all colloidal solutions the dispersed phase contains adsorbed material on the surface of the colloidal particles. The phenomenon of adsorption is in fact a very general and important one. (Cf. XXI, 10.)

5. Adsorption Equilibrium.—When any freshly prepared, finely divided substance (charcoal, or filter paper, or precipitated ferric hydroxide, for example) is shaken with a solution or a gas, it adsorbs a certain amount of each of the substances present in the solution or gas, and finally reaches a state of **adsorption equilibrium** analogous to the distribution equilibrium in the case of two immiscible solutions (XIV, 5). A large amount of experimental material dealing with adsorption equilibria has shown that the following empirical equation proposed by

Freundlich[a] is a fairly satisfactory expression for the adsorption isotherm:

$$\frac{y}{m} = kC^{1/h} \tag{3}$$

where y is the amount of a given material adsorbed by m grams of the *adsorbent* and C is the concentration of this material in the (dilute) solution, when adsorption equilibrium has been attained; k and h are characteristic empirical constants.

The constant h varies in different cases between the comparatively narrow limits $h = 2$ and $h = 10$, that is, within these limits it is independent of the temperature and of the natures of the adsorbent and the adsorbed material. The constant k, however, varies over a wide range, but usually the values of this constant for a series of substances in a given solution lie in the same *relative* order irrespective of the nature of the adsorbent.[4]

6. The Optical Properties of Disperse Systems.—Many colloidal solutions have a turbid or semiturbid appearance when examined by transmitted light, while others appear to be perfectly clear. Colloidal solutions of the metals in water are frequently beautifully colored, the color for a given metal depending upon its degree of dispersion. Many of them show also a pseudofluorescence.

When a strong beam of light is sent through a colloidal solution a diffuse cone of light (the "Tyndall[b] cone") is observed when the solution is viewed from the side against a dark background. This reflected, or more accurately *diffracted*, light is plane polarized and is always produced when light passes through any medium containing particles whose diameter is small in comparison with the wave length of light. This principle of *dark background illumination* is made use of in the *ultra-microscope*, devised by Siedentopf[c] and Zsigmondy,[d] with the aid of

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[a] Herbert Freundlich. "Extraordinary" Professor of Physical Chemistry, Electrochemistry and Chemical Technology at the Technical Institute in Braunschweig, Germany.

[b] John Tyndall (1820–1893). Professor of Natural Philosophy in the Royal Institution, London.

[c] H. Siedentopf. Chief of the Microscopy Division of the Zeiss Factory, in Jena, Germany.

[d] Richard Zsigmondy (1865–). Professor of Inorganic Chemistry in the University of Göttingen, Germany.

which individual colloidal particles as small as 3 $\mu\mu$ in diameter can be seen as small points of light against the dark field.

7. Degree of Dispersion and Solubility.—The solubility of a given crystalline substance in a given liquid increases with the degree of dispersion of the crystalline substance. That is, a substance in the form of very small crystals is more soluble than the same substance in the form of larger crystalline aggregates. This is well illustrated by the experiments of Hulett[a] with barium sulphate. He found that water shaken with fine $BaSO_4$ powder dissolved 3.67 mg. of $BaSO_4$ per liter in 5 minutes, but at the end of 24 hours the dissolved $BaSO_4$ amounted to only 2.89 mg. per liter. The solution which was saturated with respect to the fine crystals was supersaturated with respect to larger ones and the excess had slowly crystallized out of the solution in the form of the larger crystals.

This behavior is taken advantage of in analytical chemistry, where it is customary to digest or boil a $BaSO_4$ precipitate with the solution for some time before filtering, in order that the fine crystalline precipitate (which would pass through the pores of the filter) may have an opportunity to dissolve in the solution and recrystallize out again in the form of the less soluble larger crystals. The curve showing the relation between size of crystal and solubility will resemble in general the graph of equation (2). (See problem 1, above.)

8. Methods of Preparing Colloidal Solutions.—Apparently any pure substance can be obtained in any desired degree of dispersion, from molecular dispersion (true solution) up to a coarse suspension whose particles settle rapidly under the influence of gravity. The details of the large variety of methods which are available for this purpose cannot be entered into here. The various methods may, however, be grouped into two classes: (1) dispersion methods and (2) condensation methods.

As examples of the first class may be mentioned (*a*) progressive mechanical division and (*b*) dispersion with the aid of the electric arc. The method of mechanical division consists in repeatedly grinding the desired substance in a mill, together with some suitable inert material, and finally taking up the product

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[a] George Augustus Hulett (1867–). Professor of Physical Chemistry at Princeton University.

with a solvent in which the inert material forms a true solution. The inert material can then be removed by dialysis. (See Sec. 15, below.) This method has been successfully employed by von Veimarn and Stein in a large number of cases.

In the case of metals, Bredig[a] found that if an electric arc between two pieces of metal be formed within a liquid, the cloud of metallic vapor sent off from the arc remains in the liquid in the form of a colloidal solution of the metal. Direct dispersion processes are frequently accompanied by and assisted by various "peptization" processes as described more fully below (Sec. 14).

The class of condensation methods includes all processes in which the dispersed phase is "precipitated" out of a supersaturated true solution. The precipitation may be the result (*a*) of lowering the temperature, (*b*) of changing the thermodynamic environment (XIII, 1), (*c*) of bringing about a chemical reaction, or (*d*) of any two or all of these processes taking place simultaneously.

THE FORMATION OF DISPERSE SYSTEMS BY CONDENSATION

9. Von Veimarn's Law of Corresponding States.—Aside from its importance as a practical means for obtaining substances in the disperse condition, the condensation method merits a rather detailed treatment because of the light which it throws upon the relationships between the different types of colloids and the conditions which control their formation and existence. The principles governing these conditions should apply to all cases where a precipitate is produced in a fluid, irrespective of the means by which the precipitation is brought about, but for the sake of concreteness we shall consider here only the production of a precipitate by a chemical reaction in a liquid.

Suppose we mix together V liters of an n-normal solution of the substance AB with V liters of an n-normal solution of the substance MN, which reacts with AB to produce nV equivalents of the *slightly* soluble substance AM and the same number of equivalents of the very soluble substance BN. The character of the AM precipitate obtained, its degree of dispersion and

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[a] Georg Bredig (1868–). Professor of Physical Chemistry at the University of Zurich, Switzerland.

general appearance, can be accurately described with the aid of a quantity which we shall call the *dispersion coefficient*, δ, of the precipitate. A great variety of experiments carried out by von Veimarn have shown that this descriptive coefficient is expressed by the following equation which holds (qualitatively, at all events) for all substances deposited as crystals by condensation out of any liquid (III, 6):

$$\delta=\frac{N_P}{S_P}\cdot\eta\cdot k_{\mathrm{AB}}\cdot k_{\mathrm{MN}}\cdot k_{\mathrm{AM}}\cdot k_{\mathrm{BN}} \qquad (4)$$

S_P is the solubility, in equivalents per liter, of the precipitated substance AM (in the aggregated condition), N_P is the number of equivalents of the precipitate AM which must be deposited out of each liter of the solution in order that its concentration shall be reduced to S_P equivalents per liter, η is the viscosity of the solution, and k_{AB}, k_{MN}, etc., are coefficients expressing the degree of complexity (either chemical or physical, or both) of the various substances (in solution) which are involved in the precipitation reaction. For substances having a comparatively simple chemical structure and which are not associated in the solution, the above equation could be written in the approximate form

$$\delta=\frac{N_P}{S_P}\eta \qquad (5)$$

These equations postulate a law, called by von Veimarn[a] *the law of corresponding states for the crystallization process*, which may be expressed in words as follows: The degree of dispersion and the general physical appearance of crystalline precipitates are always the same irrespective of the chemical nature of these precipitates, provided that the precipitation takes place under "*corresponding conditions*." The conditions of two precipitations are said to be "corresponding" when the expression on the right-hand side of equation (5) (or, more generally, equation (4)) has the same value in both precipitations. The most important quantity in these equations is the ratio $\frac{N_P}{S_P}$, which is called the *degree of supersaturation* of the solution.

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[a] Peter Petrovic von Veimarn. Director of the Laboratory of Physical Chemistry in the Institute of Mines of the Empress Catherine II, at Petrograd.

Von Veimarn has brought forward an abundance of experimental material for demonstrating the general validity of the above law. Using it as a guide, he has been able to prepare precipitates of such materials as NaCl, $BaSO_4$, $Al(OH)_3$, AgCl, AgI, and many others, with almost any desired degree of dispersion ranging *in each instance* all the way from coarse and very obviously crystalline precipitates to gelatinous precipitates and thick transparent colloidal jellies.

In order to make clear the action of the different forces which control the degree of dispersion and behavior of precipitates formed by the condensation method, we shall illustrate the application of equation (5) to the precipitation of $BaSO_4$ by means of a chemical reaction in aqueous solution. The experimental data employed will be those obtained by von Veimarn for this purpose and the interpretation and description of the results will be those given in his book,[1] to which the student is referred for further details and also for a beautiful series of photomicrographs illustrating the appearance of the different types of precipitates.

The precipitate of $BaSO_4$ is obtained by mixing together *equal volumes* of *equivalent solutions* of $Ba(CNS)_2$ and $MnSO_4$. The concentrations in the different experiments vary all the way from $\frac{n}{20{,}000}$ to $7n$, but the volumes chosen in each experiment are such that the condition $VC = \text{constant}$ is always maintained. In other words, *the total amount of $BaSO_4$ precipitated after final equilibrium is reached is the same in all of the experiments.*

For convenience in presenting and discussing the results of the experiments, the above concentration range is *arbitrarily* divided into five regions, including respectively the concentration ranges, $\frac{n}{20{,}000}$ to $\frac{n}{7000}$, $\frac{n}{7000}$ to $\frac{n}{600}$, $\frac{n}{600}$ to $0.75n$, $0.75n$ to $3n$ and $3n$ to $7n$, approximately. Since the solubility of $BaSO_4$ in water at room temperature is about 10^{-6} equivalents per liter, these ranges correspond to the following degrees of supersaturation: 0 to 3, 3 to 48, 48 to 21,900, 21,900 to 87,600 and 87,600 to 204,000, respectively.

10. Precipitation from Solutions having Small Degrees of Supersaturation. (*a*) **Range I. Concentrations between $\frac{n}{20{,}000}$**

and $\frac{n}{7000}$. Values of $\frac{N_P}{S_P}$ between 0 and 3.—The $BaSO_4$ molecules produced by mixing these extremely dilute solutions will be distributed through a very large volume of liquid. The number of crystal nuclei (VII, 1) which can form will therefore be comparatively small and they will be very far apart. The solubility of these first crystal nuclei will, moreover, be almost equal to the concentration of the solution surrounding them (XXV, 7), and they will hence (see equation (14), XXI) have very little tendency to grow and are likely to be frequently broken up by the collisions which they will experience owing to their rapid Brownian movement (IX, 1). At a few points in the solution, however, especially around dust particles or inequalities such as scratches on the surface of the containing vessel, a few crystal nuclei of large size and hence smaller solubility and less mobility will be formed. These will be comparatively stable and will grow slowly into larger crystals.

The final result of the precipitation under these conditions will thus be the production, after a very long period of time, of a comparatively small number of coarse crystals. The smaller the degree of supersaturation the longer will be the time required for complete precipitation and the larger and fewer in number will be the crystals finally obtained. For concentrations lying between $\frac{n}{20,000}$ and $\frac{n}{10,000}$ several years would probably be required before the appearance of any precipitate could be detected. The large $BaSO_4$ crystals found in nature are probably produced in this way. Large crystals are also produced when the two solutions are mixed together very gradually, the mixing process extending over months or years.

(*b*) **Range II. Concentrations between $\frac{n}{7000}$ and $\frac{n}{600}$. Values of $\frac{N_P}{S_P}$ between 3 and 48.**—The precipitate obtained in this region consists of a fine powder which under the microscope is seen to be composed of small perfectly formed individual crystals. At $C = \frac{n}{7000}$, about a year is required for precipitation. At $C = \frac{n}{5000}$ to $\frac{n}{4000}$, a precipitate appears at the end of a month. At $C=\frac{n}{3000}$, an opalescence appears after 6–8 hours and precipitation is nearly complete at the end of 24 hours. At $C=\frac{n}{2000}$, the opalescence appears after 2–3 hours and 10–12 hours are required for the completion of the precipitation. At $C=\frac{n}{1000}$, opalescence appears in 3–5 minutes and the precipitation continues through 2–3 hours. At $C=\frac{n}{500}$, opalescence is observed after a few seconds and the precipitation is nearly complete at the end of an hour. The degree of dispersion of the precipitate increases steadily with increasing concentration of the two precipitating solutions. The initial appearance of the precipitate in the form of a very large number of very small crystals, as the value of N_P increases, is due to the fact that the chances of formation of crystal nuclei obviously increase under these conditions.

(*c*) **Suspension Colloids or Suspensoids.**—When N_P is great enough the large number of nuclei formed in the solution give it a perceptible opalescence (see above, Sec. 6) and we have a typical example of a colloidal solution of the type known as a **suspension colloid** or a **suspensoid.** When water is the dispersion medium this type of colloid is also sometimes called a **lyophobic colloid.** The disperse phase is called a **sol,** or in water a **hydrosol.**

The most general distinguishing characteristics of this type of colloid seem to be the relatively small per cent. of disperse material in the system and the fact that the solution will, under suitable conditions, exhibit the phenomenon of cataphoresis. (See below, Sec. 12*a*.) As will appear more clearly later (Sec. 11*c*), however, no sharp distinction can be drawn between the suspension colloids and the emulsion colloids or gels, or between either type of colloid and a true solution, since they shade off gradually into one another.

(*d*) **The Stability of Suspension Colloids.**—In the case of the $BaSO_4$ sol produced in the experiments described above, the stability of the colloidal solution is not very great. The small colloidal crystals gradually dissolve in the dispersion medium and recrystallize out as larger ones, which then fall to the bottom of the vessel in a fine powder. This "molecular recrystallization" is also assisted somewhat by a process of "*aggregation crystallization*" which consists in a direct union of the small crystals to form larger ones. It is thus clear that anything which will decrease the rate at which these two processes occur will increase the stability of the suspensoid.

Decreasing the solubility of the $BaSO_4$ in the dispersion medium (by pouring alcohol into the solution, for example) will evidently retard the recrystallization process and will in fact give a very stable $BaSO_4$ sol. It is for a similar reason that an AgI sol prepared by precipitation in aqueous solution is much more stable than the corresponding $BaSO_4$ sol. The stability of a sol can also obviously be increased by increasing the viscosity of the solution in which it is formed or by adding to the solution something which is adsorbed by the colloid particles so as to partially cover them and protect them against the solvent action of the dispersion medium. Or the adsorbed substance (especially if it is an ion) may actually lower the solubility of the dispersed substance. The presence of an electric charge on the particles will also prevent almost entirely the process of "aggregation crystallization." Decrease in temperature frequently increases stability also because the solubility of the sol is usually thereby decreased while the viscosity of the dispersion medium is at the same time increased.

The suspensoid stage in condensation processes can be realized (in principle, at least) for every substance which can be produced by precipitation from a liquid. All that is necessary is to make the precipitation under the conditions which define the desired dispersion coefficient. These conditions are described by equation (4) or in simple cases by equation (5). It is thus clear that suspension colloids do not represent any particular class or kind of substances. Instead they correspond simply to a condition of dispersion which can be realized (at least in principle) with *any substance whatever*.

(*e*) **Range III. Concentrations between $\frac{n}{600}$ and 0.75n. Values of $\frac{N_P}{S_P}$ between 48 and 22,000.**—The precipitates obtained in this range of concentrations are secondary growths, such as needles, skeletons and star-shaped masses. The suspensoid stage has only a very brief existence and is entirely inappreciable at the higher concentrations. At $C=0.75n$ the small needle-shaped crystals can barely be recognized as such under highest powers of the microscope.

11. Precipitation from Solutions having Large Degrees of Supersaturation. (*a*) **Range IV. Concentrations between 0.75n and 3n. Values of $\frac{N_P}{S_P}$ between 22,000 and 87,600.**—As the concentrations of the solutions increase within this range, the precipitate, at first granular, becomes curdy, then flaky and finally gelatinous in character. These so-called *amorphous* precipitates (Cf. VII, 3) are, however, composed of crystals too small to be identified even with the highest powers of the microscope, as von Veimarn has succeeded in proving.

(*b*) **Range V. Concentrations between 3n and 8n. Values of $\frac{N_P}{S_P}$ between 87,600 and 204,000.**—The drops of the $Ba(CNS)_2$ solution which fall into the $MnSO_4$ solution cover themselves quickly with a clear transparent gelatinous membrane which gradually clouds up and then falls to pieces in a voluminous flaky cloud of precipitate. At $C=4n$, this cloudiness appears very quickly. At $C=5n$, the drops settle to the bottom and if the solution is shaken or stirred, it *sets* completely to a stiff jelly. This behavior is even more pronounced at $C=6n$ and at $C=7n$ and the jelly remains clear and transparent for hours, but eventually clouds up and falls to pieces in a white cloud of flaky precipitate, owing to the gradual decrease in the degree of dispersion, resulting in this instance almost entirely from the process of "aggregation crystallization."

If the $Ba(CNS)_2$ solution is added drop by drop without shaking, the drops, covered with the transparent gelatinous membrane, collect in the bottom of the vessel in the form of a coarsely cellular jelly. The gelatinous cell walls in this jelly constitute semipermeable membranes (XII, 7). Osmosis through these gelatinous walls therefore takes place and the whole mass swells up and appears to suck up all or a large part of the liquid in the vessel, like a sponge. This phenomenon of **"swelling"** in contact with liquids is exhibited by many colloidal gels. The ordinary rubber cement of commerce is produced by allowing rubber, which is a colloidal gel, to "swell" in contact with benzene or other suitable liquid.

(*c*) **Emulsion Colloids.**—A colloid whose solutions possess the power of gelatinizing or forming a jelly (more especially if the process is reversible with respect to the temperature) is frequently called an **emulsion colloid** or an **emulsoid.** These terms are rather loosely used, however, and according to von Veimarn should be restricted to colloidal solutions in which the particles of the sol are in the liquid state of aggregation. The high concentration of the disperse phase and the high viscosity imparted to the solution seem to be the most common characteristics of the type of gel-forming colloids. Many organic substances, such as gelatine, agar-agar, and albumin, form colloidal solutions of this character in water. They are also called **lyophilic colloids** and **hydrogels.**

In this case also it should be remembered, however, that in principle *any substance whatever* can be obtained in the form of a jelly by condensation under the proper conditions. The substances, such as gelatine and agar-agar, which we most commonly associate with this gel formation do not constitute a particular class of substances in this respect, but rather a gel or an emulsion colloid represents a condition of dispersion and concentration which any substance may assume. Similarly gelatine, agar-agar, and other like substances can and have been obtained in the form of typical suspension colloids and some of them even in the form of comparatively coarse crystals. The behavior of emulsoids is considered further below.

THE PROPERTIES AND BEHAVIOR OF COLLOIDAL SOLUTIONS

12. The Electrical Properties of Colloids. (*a*) **Cataphoresis.**—By the adsorption of ions of electrolytes present in the dispersion medium and in some instances apparently by ionization of the colloid itself, the particles of a colloidal solution are often electrically charged (either positively or negatively) and the solution may therefore possess a higher conductance than the dispersion medium (the "intermicellular liquid") alone. The particles of the disperse phase will therefore behave like ions and will migrate through the solution under the influence of an

E.M.F. This electrical migration is called **cataphoresis** and can be advantageously employed in many cases to concentrate and partially separate the disperse phase from the bulk of the dispersion medium.

(*b*) **Coagulation by Electrolytes.**—If to a solution of a suspensoid an electrolyte be added, the two ions of the electrolyte will be adsorbed by the suspensoid particles, but both ions will not be adsorbed to the same extent. With increasing concentration of the electrolyte a point will therefore eventually be reached where the original charge of the colloidal particles will become neutralized by the adsorption of the oppositely charged ions of the added electrolyte. As this point is approached the stability of the sol decreases and at a certain definite concentration of the added electrolyte, coagulation and precipitation of the sol will take place. (Cf. Sec. 2.) The optimum *coagulating-concentration* of the electrolyte is more sharply defined the more uniform in size the particles of the sol are, and its value varies with the nature of the sol and the nature of the added electrolyte. The coagulating powers of electrolytes as a rule increase rapidly with the valence of the active ion. Thus the alkali cations are usually all about equally efficient in coagulating a negative colloid, but the efficiency of Ba^{++} and still more that of Al^{+++} is much greater. This is illustrated by the data in Table XXX.

TABLE XXX

Concentrations (in milli-moles per liter) of various electrolytes required to coagulate 1.9 grams of the negative colloid, As_2S_3. Experiments by Freundlich.

KCl	49.5	$MgCl_2$	0.717	$AlCl_3$	0.093
KNO_3	50.0	$CaCl_2$	0.649	$Al(NO_3)_3$	0.095
NaCl	51.0	$BaCl_2$	0.691		
LiCl	58.4	$Ba(NO_3)_2$	0.687		
HCl	30.8				

Whitney[h] and Ober found that the amounts of the coagulating ion adsorbed by coagulated arsenic trisulphide were in the ratio of the equivalent weights of the metals constituting the ions, thus indicating that the neutralization of the electric charge on the colloid particles is the factor responsible for the coagulation.

[h] Willis Rodney Whitney (1868–). Director of the Research Laboratory of the General Electric Company, Schenectady, N. Y.

The coagulation of *suspensoids* by electrolytes is a reversible process, that is, on washing out the adsorbed electrolyte, the suspensoid goes into solution again. The coagulation of the *emulsoids*, on the other hand, is frequently irreversible or difficultly reversible and usually requires much larger quantities of the electrolyte.

Colloids of opposite signs also possess the power of coagulating each other when their solutions are mixed together. Thus coagulation takes place when a solution of the positive suspensoid ferric hydroxide is mixed with a solution of the negative suspensoid arsenic trisulphide. Coagulation by heating, cooling, and by evaporation of the dispersion medium also occurs.

13. Protective Colloids.—Emulsion colloids, such as agar-agar and gelatine, when coagulated by evaporating off the water will dissolve again on the addition of water, while the suspension colloids, such as the metal hydrosols, when treated in the same way do not pass into solution again. A distinction between "reversible" and "irreversible" colloids is sometimes made on this basis. The addition of a small quantity of a reversible colloid to a solution of an irreversible colloid confers upon the latter the property of reversibility. It also renders it more stable in every way, even protecting it to a considerable extent against the coagulating effect of electrolytes. The protective action is probably due to the formation of an adsorption layer of the emulsion colloid over the surface of the particles of the suspension colloid. The use in this way of "*protective colloids*" for increasing the stability of solutions of suspensoids is a very important one and finds frequent application. Thus the gelatine on a photographic plate acts as a protective colloid for the silver chloride sol.

The relative amounts of different protective colloids necessary in order to protect a standard gold hydrosol against coagulation by a standard NaCl solution are called the "*gold numbers*" of the protective colloids. These gold numbers vary all the way from 0.005 for gelatine to 12 for potato starch.

14. Peptization.—When a finely divided coagulated precipitate, such as AgCl, is brought into contact with an aqueous solution containing a suitable substance at the proper concentration, it will pass into solution again as a colloid. This process, which is the reverse of coagulation, was given the name **"peptization"** by Graham,[a] because of its apparent analogy to the solvent action of the digestive fluids. It is not infrequently made use of in preparing colloidal solutions. According to von Veimarn the process of peptization is governed by the following conditions: (1) The particles of the precipitate to be peptized must be sufficiently small. (2) The peptizing substance must possess the property of forming a soluble compound or complex with the precipitate, and this compound must be in equilibrium with its dissociation products in the solution. (3) The precipitate must be practically insoluble in the absence of the peptizing material. Thus a precipitate of AgI can be peptized by a solution of KI. The most effective concentration of the KI for this purpose is about $0.03n$.

15. Dialysis and Ultrafiltration.—The property possessed by the colloidal jellies and by many membranes, such as parchment paper and gold-beater's skin, of acting as semipermeable membranes is made use of in removing impurities, such as electrolytes and other substances, which may be present as solutes in the dispersion medium of a colloidal solution. When this process of purifying the colloid is carried out by simply allowing the impurities to diffuse through the membrane into the pure dispersion medium on the other side, the process is known as **dialysis.**

By impregnating a supporting medium, such as filter paper, with a solution of a suitable colloidal jelly (as for example an acetic acid solution of collodion) filters of different degrees of porosity can be prepared. These *ultrafilters*, as they are called, have been used for separating colloidal particles of different degrees of dispersion from one another.

16. Some Properties of Emulsion Colloids and Solutes of very High Molecular Weight.—According to the theory of von Veimarn any substance will be obtained in the form of a clear transparent colloidal jelly, if a sufficiently large quantity of it is precipitated in any way from a small volume of a medium in

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[a] Thomas Graham, F.R.S. (1805–1869). Professor of Chemistry in the University of London. The pioneer investigator in the field of colloid chemistry. He divided substances into *colloids* and *crystalloids* on the basis of their tendencies to diffuse or dialyze. He was also one of the earliest investigators of the phenomenon of adsorption.

which its solubility is sufficiently slight. The individual colloidal particles of these gels are so small, that is, they consist of so few molecules, that the adsorbed layer of dispersion medium upon the surface of each particle constitutes relatively such a considerable proportion of the particle as to confer upon it to an appreciable degree the properties of a liquid particle. For this reason it is frequently very difficult to decide in a given case whether the particles of the gel are in the crystalline state of aggregation or in the liquid state of aggregation, and indeed with increasing degree of dispersion the one state may pass gradually over into the other and the distinction loses its significance. If a decrease in degree of dispersion results in the formation of an emulsion (Sec. 3), the gel would be classed as a true emulsoid. On the other hand, if a suspension or a precipitate of small crystals resulted, the gel would be more properly called a pseudo-emulsoid, if indeed the term emulsoid should be applied to it at all.

True emulsoids are usually more stable than pseudo-emulsoids owing to the absence of crystal forces which cause the particles of the latter to gradually increase in size. Some pseudo-emulsoids composed of complex organic substances are also very stable owing to the weakness of the crystal forces. Lowering the temperature will obviously increase the stability of a gel composed of crystalline particles, and the more the surface of the colloidal particles is contaminated with adsorbed impurities, the more difficult will it be for the crystal forces to act and render the gel unstable. A typical example[1] of gelatinization by fall in temperature occurs in cooling a hot saturated solution of chrome-alum. The solution gradually increases in viscosity as the temperature falls and eventually sets to a stiff transparent jelly which on heating again passes gradually over into solution. A similar behavior is shown by the more stable gels, agar-agar and gelatine.

The behavior of agar-agar solutions and many other organic gels of high molecular weight is frequently very much complicated by the fact that the sol is not a pure substance but a mixture of closely related substances. Thus an agar-agar solution consists[2] of at least two substances, α-agar-agar and β-agar-agar, which go over into each other under different conditions. The α-agar-agar (which can be obtained by precipitation with alcohol from a water solution) is practically insoluble, as such, in water. On warming with water, however, it gradually changes over into the very soluble β-form and thus passes into solution. Owing to this gradual change of one of these forms into the other, the properties and behavior of an agar-agar solution depend to a pronounced degree upon the previous history of the solution. The same is true of gelatine solutions.

Molecularly dispersed, and therefore "true," solutions of substances of very high molecular weight display many of the properties of colloids (including the property of gel formation) owing to the fact that the individual molecules are so large. In fact a series of solutions of the sodium salts of the fatty acids of progressively increasing molecular weight shows a continuous series of properties ranging from true solutions, displaying no colloidal properties, to typical colloidal solutions. The colloidal behavior of solutions of the higher members of the series is due, however, in a large measure to the hydrolysis of the salt which produces a colloidal solution of the insoluble fatty acid. The ordinary soap solutions are of this character.

17. Classification of Disperse Systems with Reference to Degree of Dispersion.—As pointed out in the foregoing pages, it is possible to realize almost a continuous series of systems with degrees of dispersion ranging all the way from the ordinary nondispersed heterogeneous systems to the molecularly dispersed homogeneous systems which we call true solutions. Any scheme for classifying systems with respect to degree of dispersion must therefore include and exhibit this gradual change in the character of the system which accompanies the gradual increase in degree of dispersion. The following schematic representation[5] of disperse systems from this point of view fulfills this condition. The arrangement and nomenclature are due principally to Wolfgang Ostwald[a] and to P. von Veimarn.

18. The Literature of Colloid Chemistry.—This branch of Physical Chemistry has developed with rapid strides during the

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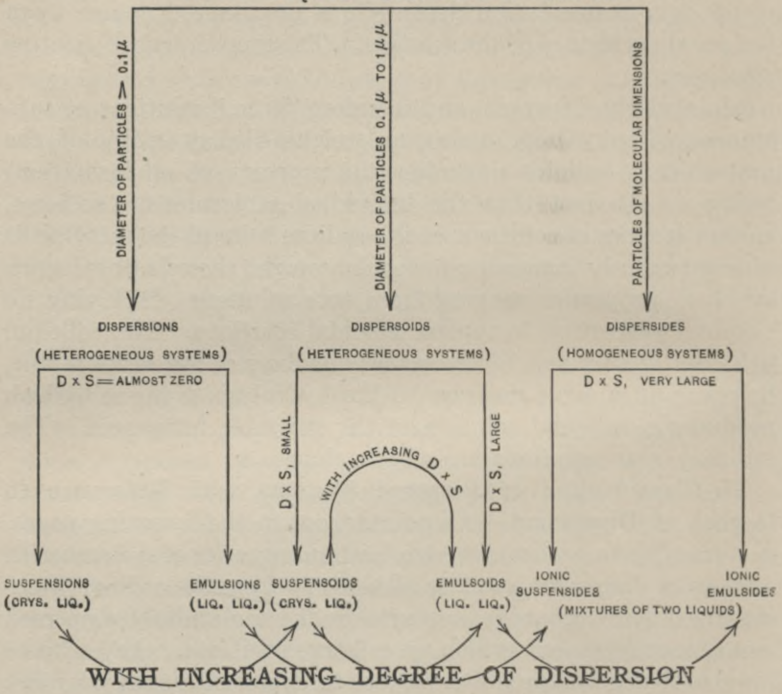
[a] Wolfgang Ostwald. A son of Wilhelm Ostwald. Privatdozent at the University of Leipzig and editor of the *Kolloid-Zeitschrift* and the *Kolloidchemische Beihefte.*

last 15 years and already possesses a formidable quantity of literature, references to which will be found in the books listed below. Of these books, that by Ostwald, is well arranged, comprehensive and clearly and attractively written. For beginners who do not read German the short sketch of the subject by Hatschek may be recommended. The other books in the list will be more readily appreciated by advanced students.

DISPERSE SYSTEMS
WITH LIQUID DISPERSION MEDIA



D = DEGREE OF DISPERSION. S = SOLUBILITY

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CHAPTER XXVI

RADIOACTIVITY

1. Radioactive Change.—In 1896 Becquerel[a] observed that the element uranium gave out a radiation or emanation of some character which was able to penetrate a sheet of metal and to affect a photographic plate. The air in the neighborhood of this "*radioactive*" matter was found to be ionized as shown by its discharging effect upon an electroscope. Shortly afterward the Curies[b] discovered two new radioactive elements, radium and polonium, in the mineral pitchblende, and Debierne[c] found a third, actinium, in the same material. Since these pioneer discoveries, many workers have entered this field and as a result of their labors some thirty new radioactive elements have been discovered.

The researches of Sir Ernest Rutherford[d] showed that the radiation given out by radioactive substances consists of three distinct classes of rays, which he named α-, β-, and γ-rays, respectively. He also advanced the theory, which all subsequent research has confirmed and which is now universally accepted, that the process of radioactive change is the result of a spontaneous decomposition of the atoms of the radioactive elements, as a consequence of which new elements, frequently even less stable than the parent element, are produced. (Cf. I, 2*f*.) These new radioactive elements decompose in turn and produce others, and this process continues through many stages until finally a stable element is produced as the end product of the series of changes. This stable end product appears in each case to be an isotope (I, 2*c*) of lead.

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[a] Henri Becquerel (1852–1908). Professor of Physics in the Laboratory of the National Museum of Natural History at Paris, a position formerly held by his father and grandfather and at present filled by his son.

[b] Pierre Curie (1859–1906) and his wife, Marie Curie, *née* Sklodowska, D.Sc., L.L.D. Professors of Physics at the Sorbonne, Paris.

[c] André Debierne. Investigator in Radiochemistry at the Sorbonne, Paris.

[d] Sir Ernest Rutherford, F.R.S. (1871–). Langworthy Professor of Physics in the University of Manchester, England.

2. The Nature of α-Rays.—These rays consist of a stream of positively charged particles shot out from the atom of the radioactive element with a velocity about one-tenth as great as that of light. Each particle carries *two* atomic charges of positive electricity and these particles have been proved to be helium atoms with two electrons (I, 2*e*) missing.

When α-rays are allowed to pass through any homogeneous material, they collide with the atoms in their path, ionize a certain number of them, are themselves slowed up as a consequence, and when their velocity falls to a "critical" value, which is about 2.7 per cent. of that of light, their ionizing power ceases and they can no longer be detected by electrical means. They are then said to be "*absorbed*" by the material and the distance which they cover previous to this absorption is called their "*range*." This range is proportional to the cube of the initial velocity and is a characteristic property of the radioactive element giving rise to the α-particles. The absorptive powers of different materials, whether elements, compounds or mixtures, for the α-rays have been found by Bragg to be quite closely proportional to the mean of the square roots of the atomic weights of the elements composing the absorbing material.

3. The Scattering of α-Particles.—Most of the α-particles in passing through a given material move in straight lines, but some of them are deviated in one direction or the other and this deviation or "scattering" is produced, according to Sir Ernest Rutherford, whenever an α-particle passes near enough to the nucleus of an atom to be appreciably acted upon by the electric charge of the nucleus. The magnitude of this central positive charge of a given atom is called its **atomic number,** and Sir Ernest Rutherford has calculated from measurements of the scattering effect that the nuclear positive charge of an atom is approximately equal to one-half its atomic weight multiplied by the charge of an electron. The scattering effect also indicates that practically all of the mass of an atom is concentrated in this positively charged nucleus, whose diameter in the case of hydrogen has been calculated to be only about 10^{-13} cm., the total diameter of the hydrogen atom being of the order of magnitude of 10^{-8} cm.

4. The Nature of the β-Rays.—The β-rays consist of a stream of electrons moving with velocities ranging up to a maximum almost equal to the velocity of light. While all the α-particles shot out by the decomposing atoms of a given radioactive element move with the same velocity, the β-rays consist of particles moving with a great variety of velocities.

The ionizing power of the β-rays is much weaker than that of the α-rays. Their penetrating power increases with their velocity and is very great for the very rapid ones. They are most conveniently detected with the aid of the photographic plate.

5. The Nature of the γ-Rays.—These rays are identical with X-rays, that is, they are ordinary light rays of extremely short wave lengths. The wave length varies from about 10^{-8} cm. for the "soft" or feebly penetrating rays to $0.7 \cdot 10^{-9}$ cm. for the "hard" or very penetrating rays. Since these rays do not consist of charged particles they are not deflected by electromagnetic or electrostatic fields as are the α- and β-rays.

6. The Radioactive Constant and the Period of Half Change.—The number of atoms of a radioactive element which decompose per second at any time t is proportional to the number in existence at that time, or mathematically (Cf. equation 6, XXI),

$$-\frac{dn}{dt} = \lambda n \qquad (1)$$

where λ, the proportionality constant, is called the **radioactive constant** and is an important characteristic of the decomposing element. The reciprocal of this quantity is called the **average life period** of the element, and the time required for one-half of a given quantity of a radioactive element to decompose is called its **period of half change** or its **half-value period.**

Problem 1.—Show that the period of half change of a radioactive element is equal to $\frac{0.6932}{\lambda}$.

The periods of half change of the different radioactive elements vary all the way from thousands of millions of years for the longest lived primary elements to less than a millionth of a second for the shortest lived one.

An important empirical relation between the radioactive constant and the range R of the α-particles emitted by a decomposing element has been discovered by Geiger and Nuttall. This rela-

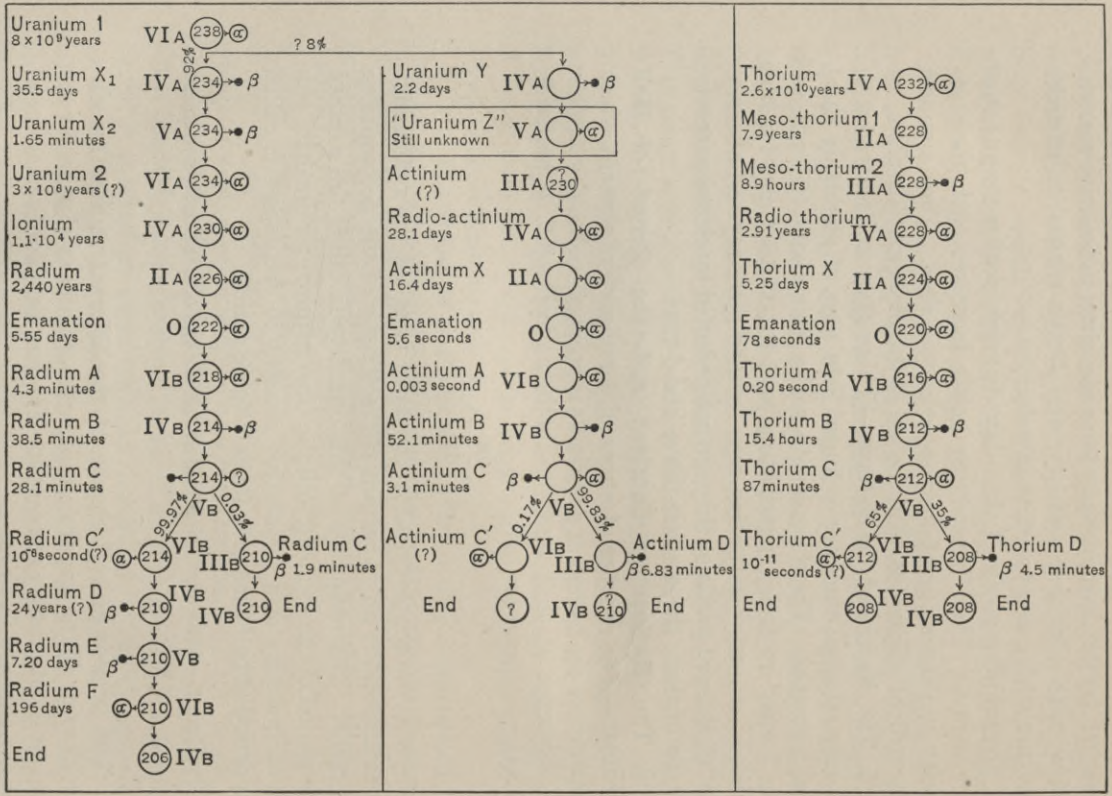

FIG. 55.—The Radioactive Disintegration Series as Arranged by Soddy. Reproduced, by permission of Longmans, Green & Co., from Soddy's *The Chemistry of the Radio-elements.*

tion is expressed by the equation

$$\lambda = aR^b \tag{2}$$

where b is a general constant and a is a constant characteristic of the series to which the element belongs. This relationship is especially valuable for the calculation of the radioactive constants of the very long or very short lived elements for which most of the other methods fail.

7. The Disintegration Series.—Probably all of the thirty odd radioactive elements are decomposition products of one of the two parent elements, uranium and thorium. In order to show the chief characteristics of the radio-elements and their relations to one another, it is customary to arrange them in a **disintegration series** starting with the parent element and showing all the successive steps in its disintegration up to the production of the stable end product of the series.

Fig. 55 shows the three disintegration series as arranged by Soddy. The numbers in the circles are the atomic weights of the elements. The nature of the rays (whether α or β) given out in each decomposition is indicated by the small circles or dots at the side of the larger circles. The Roman numerals indicate the group to which the element belongs in the periodic system, and hence from these numerals the chemical properties of the element can be inferred. Below the name of each element appears the value of $1/\lambda$, the "average life period" of the element.

8. Radioactive Equilibrium.—A radioactive material is said to be in radioactive equilibrium when the rate of production of each radioactive element from its parent is just balanced by its rate of decomposition into the next lower element of the series. The equilibrium quantities of the different elements in any such radioactive material are inversely proportional to their radioactive constants.

9. Counting the α-Particles.—When an α-particle strikes a screen covered with zinc sulphide (such a screen is called a *spinthariscope*), it produces a small flash of light which is easily visible under a microscope. By counting the number of flashes observed on such a screen, one can find the number of α-particles which strike it in a given period of time. Instead of the spinthariscope an ionization vessel may also be employed for the same purpose. An apparatus arranged for this purpose by Rutherford and Geiger is shown in Fig. 56. The radioactive material was placed upon a suitable support (not shown) in the evacuated tube, E, at a known distance, R, from the small opening, D, of known area, A. This opening consisted of a thin mica plate through which the α-particles could pass without difficulty into the detecting vessel, B, which was filled with air at a low pressure and was provided with two electrodes charged at a high potential and connected to a sensitive electrometer, an instrument for indicating the passage of a current. Hence whenever an α-particle passed through the small opening at D into the detecting vessel, it ionized the air and a momentary current of electricity flowed from one of the electrodes to the other and the passage of this current was indicated by a sudden throw of the electrometer needle. The observer has only to count the number of throws of the electrometer needle which occur in a given time interval and he has at once the number of α-particles which passed through the area D in that time; or the throws of the galvanometer may be registered photographically on a moving film, if desired. Knowing the area of the opening D and its distance from the radioactive source, it is easy to compute the *total* number of α-particles given off by the radium in that time, for they are given off uniformly in all directions. In this way, Rutherford and Geiger found that the α-particles are given off by radium at the rate of about $107 \cdot 10^{16}$ (± 3 per cent.) particles per year, per gram of radium.

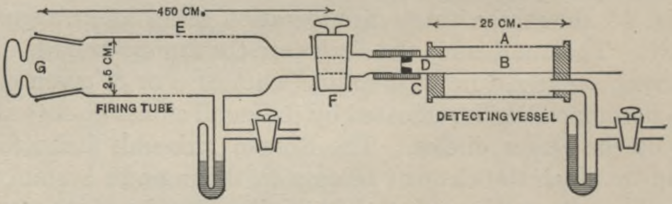

Fig. 56.—Rutherford and Geiger's Apparatus for Counting the α-particles.

In a similar way, but using a spinthariscope and microscope in place of the ionization vessel, Regener has determined the rate of emission of α-particles from polonium. About 20,000 particles in all were counted in the different experiments and the average of all experiments gave a rate of emission of $3.94 \cdot 10^5$

(± 0.3 per cent.) α-particles per second. By collecting the α-particles in a suitable measuring vessel the total charge carried by them was also determined by Regener. This charge was found to be $37.7 \cdot 10^{-5}$ electrostatic units for the α-particles shot out from the polonium in 1 second.

10. The Rate of Production of Helium by Radium.—Rutherford and Boltwood[a] carefully collected and measured all of the helium (10.38 ± 0.05 cu. mm.) produced from a sample of radium in 4 months and found in this way that the helium produced by the decomposition of the radium atoms amounted to 39 cu. mm. per year, per gram of radium.

11. The Calculation of Avogadro's Number from Radioactive Data.—By combining Rutherford and Geiger's value for the rate of emission of α-particles by radium with Rutherford and Boltwood's value for the rate of production of helium from radium, the value $(61.5 \pm 2)10^{22}$ is obtained for Avogadro's number. Similarly Regener's value for the rate of emission of α-particles by polonium, combined with his determination of the total charge carried by these particles, gives $(60.5 \pm 2) \cdot 10^{22}$ for the value of this constant. These values agree, within the accuracy of the measurements involved, with the value of this constant computed by more accurate methods of entirely different character. (Cf. IX, 3 and 4, and XVI, 6.)

Problem 2.—Carry out the calculations indicated above.

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[a] Betram Borden Boltwood (1870–). Professor of Radiochemistry at Yale University.

CHAPTER XXVII

ATOMIC STRUCTURE AND THE PERIODIC SYSTEM

1. The Structure of the Atom.[1, 2, 3]—As a result largely of investigations published since 1912, a theory of atomic structure has been evolved which is able to interpret satisfactorily a considerable number of important relationships concerning the chemical elements. According to this theory every atom is supposed to be made up of a positively charged nucleus, in which most of the mass of the atom resides, surrounded by rings of revolving electrons. The nucleus is itself composed of a definite number of *units* of positive electricity associated with a certain number of nuclear electrons, the positive electricity being always in excess, however. The elementary units of positive electricity are supposed to be identical with the nucleus of the hydrogen atom, that is, they are hydrogen atoms minus one electron each.

The mass of an atom, while due chiefly to the number of hydrogen nuclei which it contains, will not necessarily be an integral multiple of the mass of the hydrogen atom (Prout's[a] Hypothesis), because according to electromagnetic theory the total mass of a body made up of positive and negative units will depend somewhat upon the manner in which they are packed together, and upon the energy change accompanying the formation of the atom.[4] If proper allowance[5] be made for this "*packing effect*" however, a very exact multiple relationship can be shown to hold for a considerable number of elements as explained in section 4 below.

The appearance of the helium atom almost intact in so many radioactive changes indicates that the nucleus of this atom constitutes a secondary unit of positive electricity of great stability. The nucleus of the helium atom, or an α-particle in other words, is supposed to be made up of four hydrogen nuclei united with two nuclear electrons.

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[a] William Prout (1785–1850). An English physician.

Since an atom as a whole is electrically neutral, the positive charge carried by its nucleus must be equal to the number of electrons exterior to the nucleus. This number is called the **atomic number** of the element and is a very important and characteristic constant, more characteristic even than its atomic weight, since the principal physical and chemical properties of the elements are determined by their atomic numbers, not by their atomic weights. Starting with hydrogen, the atomic numbers of the elements run from H = 1, He = 2, C = 3, O = 6, etc., up to U = 92.

2. Atomic Numbers and X-Ray Spectra.—A very important and valuable relation connecting the atomic number of an element with its X-ray spectrum has been discovered by Moseley.[a] The spectrum of the characteristic X-ray radiation (VIII, 4) of an element is very simple, consisting of two groups of lines called the "K" radiation and the "L" radiation, respectively. Moseley has made a systematic study of the "K" radiations of the elements from Al to Au and has found that these radiations consist of two strong lines whose frequencies (ν) increase with increasing atomic weight of the element in accordance with the very simple relation,

$$\nu = k(\mathbf{A}_N - 1)^2 \tag{1}$$

where k is a constant and $\mathbf{A}_N$ is the atomic number of the element.

This relation gives us an exceedingly convenient and rapid method for determining the atomic numbers of a large number of elements and Moseley's arrangement of the elements in accordance with his determinations of their atomic numbers in this manner has brought to light several interesting relationships which will be discussed below in connection with the consideration of a periodic system of the elements arranged in accordance with Moseley's determinations of their atomic numbers.

3. The Radio-elements and the Periodic System.[1]—For a long time the relation of the radio-elements to the periodic system remained an unsolved problem, but in 1913 the solution of the problem was finally obtained through the independent effort of Fajans, Soddy and others, who perceived an important generalization with regard to the changes in chemical properties resulting

[a] H. G. T. Moseley. Fellow at the University of Manchester, England.

from successive steps in a radioactive disintegration. This generalization is in complete accord with, and a necessary consequence of, the theory of atomic structure outlined in section 1. It may be formulated in terms of that theory as follows:

1. In a radioactive transformation in which α-particles are expelled, the resulting new element must be composed of atoms with a nuclear charge 2 units less and with an atomic weight approximately 4 units less (Cf. Fig. 55) than that of the parent element. The atomic number therefore undergoes a decrease of 2 units and the new element will occupy a position in the periodic system two groups lower down than the one occupied by its parent.

2. In a β-ray decomposition the atomic weight of the new element will be practically the same as that of its parent, since the mass of the electron lost is a negligible portion of the mass of the whole atom. (Cf. Fig. 55.) This electron comes from the nucleus of the parent atom, however, so that the nuclear charge and thus the atomic number of the new element will be 1 unit larger than that of its parent and it will thus occupy a position in the periodic system one group higher up than its parent.

By means of this simple generalization the atomic numbers and the chemical and physical properties of all the elements of a given disintegration series can be predicted, if the atomic number of one of the elements is known. The arrangement of all the known radioactive elements is the Mendelejeff table in accordance with the above scheme as shown in Fig. 57. If we start with the radium series, for example, we find U_1, an element in Group 6A. It undergoes an α-ray disintegration and produces $U\text{-}X_1$, an element belonging to Group 4A. This in turn undergoes β-ray decomposition and produces $U\text{-}X_2$ which belongs to Group 5A, etc., the final product being an element in Group 4B. The atomic numbers of the elements are shown at the bottom of the table.

The most striking feature of this table is the fact that a single place in the periodic system is filled by several different elements. Thus the place occupied by Pb in the table is also filled by Ra–B, Ra–D, Th–B, and Ac–B, together with five other unnamed elements which are the stable end products of the different disintegration series. These other elements are all *isotopes* (I, 2*c*) of

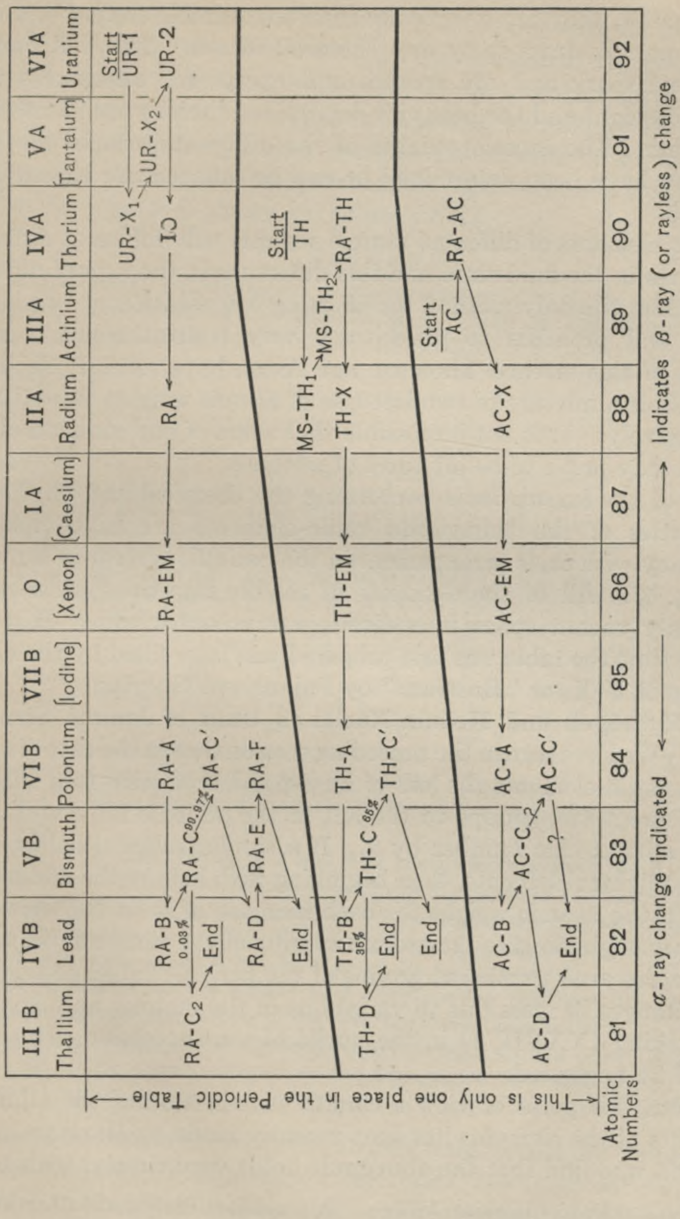

FIG. 57.—The Radio-elements and the Periodic Law. Reproduced by permission of Longmans, Green and Co., from Soddy's *The Chemistry of the Radio-elements.*

Pb, that is, they are chemically indistinguishable from Pb, and non-separable from it by any chemical means. They all have identical spark and arc spectra and except for differences in atomic weight and the behavior determined thereby are identical elements. The atomic weights of the different isotopes as far as they have been determined or can be inferred are shown in Fig. 55.

Two elements of different atomic weights will diffuse at different rates in the fluid state and this difference in the rate of diffusion offers the only method for effecting a separation of two isotopes and promises to yield some very fruitful results. By means of this method Thomson and Aston have recently shown that Ne is a mixture of two isotopes of atomic weights 20 and 22 respectively. It is not impossible that some of our common elements may prove to be mixtures of isotopes.

All of the known facts concerning the chemical and physical properties of the thirty odd radio-elements are in complete harmony with their arrangement in the periodic system as shown in Fig. 57. All of the elements fit readily into the system and the only vacant space in a disintegration series which existed at the time the table was first prepared was later filled by the discovery of U-X_2 or "Brevium" by Fajans and Göhring.

4. Hydrogen and Helium Nuclei as Units of Atomic Structure.—We have seen in the preceding section that in the case of the heavy radio-elements the loss of an α-particle of mass four shifts the element two groups to the left in the periodic table and decreases its atomic number by 2. If a similar relation held true for the lighter elements, then beginning with helium the addition of 4 to the atomic weight for each increase of 2 in the atomic number ought to give the atomic weights of the elements belonging to the even numbered groups of the periodic table, provided the changes in mass due to variations in the manner and degree of packing (XXVII, 1) in the nuclei of the successive elements could be neglected.

From this point of view a careful examination of the atomic weights of the elements has been recently made by Harkins[a] and Wilson who find that the above rule holds very closely, with but

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[a] William Draper Harkins (1873–). Assistant Professor of Chemistry the University of Chicago.

few exceptions, for all the elements with atomic weights less than 60. A similar rule also holds for the elements of the odd-numbered groups in the periodic table, if the assumption is made that the first of these elements, lithium, is built up from one helium and three hydrogen nuclei. The results of this point of view and the agreement between the observed and calculated atomic weights is shown in Table XXXI.

TABLE XXXI

A symbolical representation of the atomic weights of the elements in the first three series of the periodic table. [Harkins and Wilson, Jour. Amer. Chem. Soc., **37,** 1391 (1915).] $H=1.0078$.

	0	1	2	3	4	5	6	7	8	
	He	Li	Be	B	C	N	O	F		
Ser.2.	He	$He+H_3$	$2He+H$	$2He+H_3$	$3He$	$3He+H_2$	$4He$	$4He+H_3$		
Theor.	4.00	7.00	9.0	11.0	12.00	14.00	16.00	19.00		
Det .	4.00	6.94	9.1	11.0	12.00	14.01	16.00	19.00		
	Ne	Na	Mg	Al	Si	P	S	Cl		
Ser. 3.	$5He$	$5He+H_3$	$6He$	$6He+H_3$	$7He$	$7He+H_3$	$8He$	$8He+H_3$		
Theor.	20.0	23.00	24.00	27.0	28.0	31.00	32.00	35.00		
Det...	20.0	23.00	24.32	27.1	28.3	31.02	32.07	35.46		
	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
Ser. 4.	$10He$	$9He+H_3$	$10He$	$11He$	$12He$	$12He+H_3$	$13He$	$13He+H_3$	$14He$	$14He+H_3$
Theor.	39.9	39.00	40.00	44.0	48.0	51.0	52.0	55.00	56.00	59.00
Det...	40.0	39.10	40.07	44.1	48.1	51.0	52.0	54.93	55.84	58.97

Increment from Series 2 to Series 3 = $4He$. Increment from Series 3 to Series 4 = $5He$ ($4He$ for K and Ca). Increment from Series 4 to Series 5 = $6He$.

"This table gives Series 2, 3 and 4 of the periodic system, built up by adding the weight of one helium atom for each change of two places to the right, and by adding enough multiples of the weight of a hydrogen atom to make up the atomic weight. In order to make the relationship apparent a symbolical representation has been used, He being taken to stand for the weight 4, and H for the weight 1.00. Built up in this way, the atomic weights of all of the members of the even numbered groups (with the exception of beryllium) may be represented by a whole number of symbols He, while all of the atomic weights in the odd groups [with the exception of chlorine] may be represented by $3H$ plus a whole number of symbols He."

It will be noted that while the atomic weights marked "Theor." in the table are computed on the basis $H=1$, those marked "Det." are the directly determined values on the basis $H=1.0078$ (*i.e.*, $O=16$). That the agreement between the two is nevertheless close is interpreted by Harkins and Wilson[5] as indicating that the packing effect in the formation of these elements from hydrogen nuclei and electrons must involve a constant decrease of about 0.77 per cent. in the mass of the resulting atom; and that nearly all of this decrease probably takes place when the helium atom is formed, which agrees with the great stability of the helium nucleus as a secondary unit of atomic structure. We thus have for the first time a reasonable explanation of the otherwise peculiar, but well-known fact that the whole-number relationship among the atomic weights is much more exact on the $O=16$ than on the $H=1$ basis. The table shows elements corresponding to all possible multiples of *He* except 2*He* and 9*He*. In place of the 9*He* we, however, find 10*He* occurring twice, as Ar and Ca.

The numerical relationships between the atomic weights of the elements displayed by Table XXXI were first discovered empirically by Rydberg[a] as early as 1886 and his paper, in fact, contains a purely empirical presentation of nearly all the periodic relationships which are today finding physical interpretations in terms of atomic structure. His mathematical representation[4] of these relationships involved certain empirical constants which are interpreted by our modern theory in terms of hydrogen and helium units, the charge on the nucleus, and the packing effect, respectively.

The relation connecting atomic weight with atomic number for the elements shown in Table XXXI can be expressed mathematically by the equation

$$\mathbf{A}_W=2\mathbf{A}_N+\tfrac{1}{2}+\tfrac{1}{2}(-1)^{\mathbf{A}_{\overline{N}}\mathbf{1}} \qquad (2)$$

Beginning with the element Ni, this relation ceases to hold accurately for the elements of higher atomic weights. Whether this failure is due to a change in the packing effect or to some other factor or factors it is impossible to say at present. The exceptional behavior of Cl, Mg, and Si remains to be explained also.

5. Graphical Representation of the Periodic Law.—A great many suggestions for improving Mendelejeff's[b] tabular representation of the periodic law have been proposed from time to time.

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[a] J. R. Rydberg. Professor of Physics, Lund University, Sweden.

[b] Dmitri Ivanovitsch Mendelejeff (1834–1907). Professor of General Chemistry in the University of St. Petersburg.

Probably the best of these suggestions are those which make use of some kind of a continuous spiral or helix, an early form of which was described by Sir William Crookes[a] in 1886. In order to bring this method of representation up to date the elements should be arranged on the helix in the order of their atomic numbers and the system should include all of the radio-elements. Two helical diagrams of this character are shown in Figs. 58 and 59, respectively.

The system shown in Fig. 58 consists of six principal or primary spirals wrapped around what might be described as a cylinder with a pear-shaped cross section, and three minor or secondary spirals wrapped on an adjacent cylinder. The purpose of the pear-shaped cross section is to contrast graphically the very rapid variation of chemical properties which occurs in passing through the transition group (Group 0) of the primary spirals with the very gradual variation in chemical properties which occurs in passing through the transition group (Group 8) of the secondary spirals.

Fig. 59 is similar in most respects to Fig. 58, but the cylinder employed has a circular cross section instead of a pear-shaped one, thus permitting the secondary spirals to be placed inside of the cylinder on which the primary spirals are wrapped and bringing the elements of subdivisions A and B of the different groups into proximity with one another. The resemblances between the elements of the two subdivisions of a given group, which in Fig. 58 are only made apparent by the lettering at the top, are thus indicated graphically by Fig. 59. The latter figure does not, however, exhibit quite so prominently the relation indicated by the pear-shaped cross section of Fig. 58, but it could evidently be readily made to do so. With these exceptions and the fact that Group 4 is, as it should be, divided into two subdivisions in Fig. 59, both figures are substantially identical and may be considered as the most modern representations of the relations involved in the periodic law.

In both figures the elements follow each other around the helix in the order of their atomic numbers, all the elements in the same subgroup being located on the same straight line or rod.

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[a] William Crookes, Knt., F.R.S. (1832–). Famous English scientist. Discoverer of the element thallium.

The end of this line or rod is lettered with the number of the subgroup which it represents. The *electro-negative elements* are represented by the black circles *on the back of the cylinder*. The *electro-positive elements* are represented by white circles *on the front of the cylinder*. The black-and-white circles represent the *transition elements* which are located *on the right- and left-hand edges of the cylinder*. The elements are spaced along the cylinder in accordance with their atomic weights, the atomic weights being plotted along an axis parallel with the axis of the cylinder. This spacing according to atomic weights does not appear to have been definitely followed in Soddy's figure but has been employed in other modifications of the Crookes' helix, which Soddy appears to have used as his starting point. Fig. 59 being the projection of a space model shows the relationship very clearly, however, the scale of atomic weights being indicated on the left-hand margin. Vacant places in the table are indicated by the omission of the symbol of the element. In Fig. 58 the isotopic elements occupying a given place are indicated only by their most familiar representative, while in Fig. 59 the separate isotopes are indicated by small circles, a similar method of representation being employed in the case of the rare earth group.

6. The Succession of the Elements in the Periodic System.— The elements in Figs. 58 and 59 follow each other in the order of their atomic numbers not in order of their atomic weights. For all of the elements between Al and Au the arrangement is based upon the values of the atomic numbers determined by Moseley as described above. This arrangement corrects several inconsistencies which existed in the old Mendelejeff arrangement. Thus nickel and cobalt in the new arrangement appear naturally in their proper order as do also iodine and tellurium and argon and potassium.

These and some of the other relationships shown by the new arrangement may be more easily appreciated by making an imaginary journey around the helix. Starting with H which seems to occupy a place by itself we come next to the inert 0-group element, He, with a valence of 0. Passing across the front of the cylinder we come next to the strongly electro-positive element, Li, with a positive valence of 1, followed by Be, with a positive valence of 2.

The 3rd-group element, B, has a rather weak positive valence of 3 and a somewhat weaker negative valence. Finally on the right side of the cylinder we come to the 4th-group transition element, C, which displays a positive valence of 4 and a negative valence of 4, both of equal strength. We now pass to the electro-negative elements on the back of the cylinder, the positive valence continuing to decrease in strength and increase in value while the negative valence increases in strength, and decreases in value, until we reach the 0-group element, Ne, on the left-hand side of the cylinder, thus completing one full loop of the principal or primary type.

It should be noted that the characteristic valence number of any element on a primary loop is obtained by counting from the 0-group, toward the front for positive elements and toward the back for negative elements. The maximum positive or oxygen valence of the element is, however, equal to its group number in every case. If the maximum positive valence exhibited by an element be numerically added to its maximum negative valence, there is evidently a tendency for the sum to equal 8. This tendency is exhibited especially by the elements of the 4th, 5th, 6th and 7th groups and is known as *Abegg's*[a] *rule*. In order to make it hold also for the electro-positive elements, Abegg assigned the proper negative valences to them, regarding these valences, however, as dormant. Thus Li is assigned a dormant negative valence of 7, and Be one of 6. The elements of the 3rd-group, however, actually exhibit a negative valence, although usually not the maximum value required by Abegg's rule.

In this connection it is interesting to note that in both of the transition groups, Group 0 and Group 4, which stand between the electro-negative elements on the back and the electro-positive elements on the front of the cylinder, the total valence value (algebraically computed) of the elements is always 0. The transition through Group 0, however, always involves an abrupt jump from a strong electro-negative to a strong electro-positive element, while in passing through Group 4 this change in properties is a very gradual one. As explained above, this behavior is indicated graphically by the shape of the loop in Fig. 58.

[a] Richard Abegg (1869–1909). Professor of Chemistry in the University of Breslau, Germany. Editor of the *Zeitschrift für Elektrochemie.*

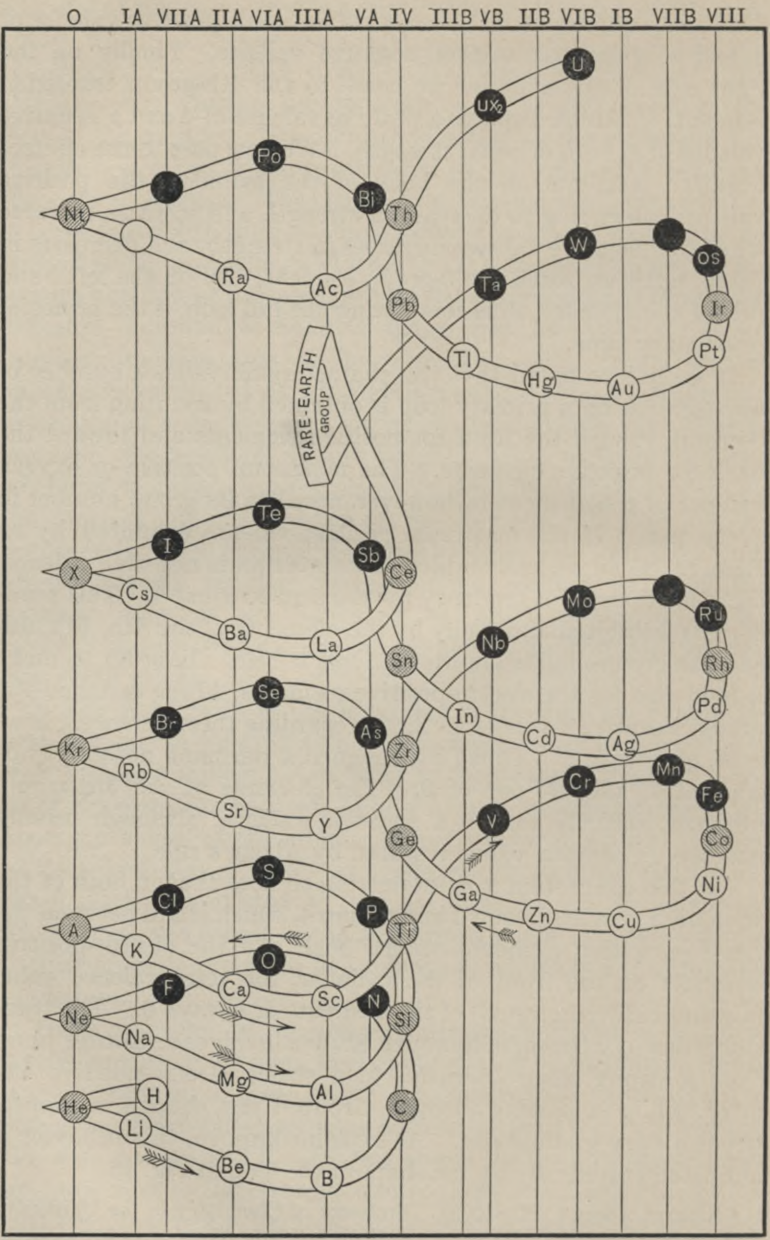

FIG. 58.—Helical Diagram of the Periodic System as arranged by Soddy. Reproduced by permission of Longmans, Green and Co., from Soddy's *The Chemistry of the Radio-elements.*

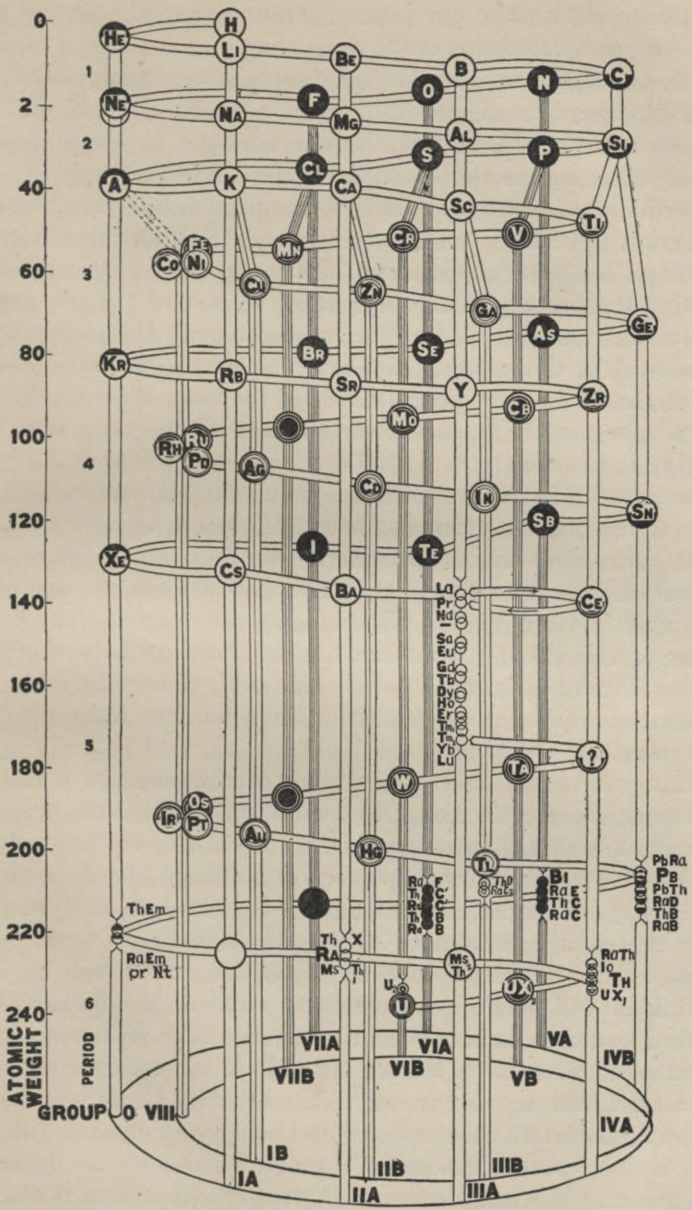

Fig. 59.—Helical Model of the Periodic System Constructed by Professor W. D. Harkins of the University of Chicago. The drawing is a vertical projection with the base shown in perspective. (Harkins, Jour. Amer. Chem. Soc. about Dec., 1915.)

Returning now to our journey around the cylinder, we find that two complete loops of the same character as the first one are made, but that in making the third loop, after passing across the front of the cylinder in the normal manner through A, K, Ca, and Sc, we find that in passing through Group 4 we enter upon a spiral belonging to the secondary type. The elements, V, Cr, Mn, which we now meet belong to subdivision B of their respective groups in each instance, instead of to subdivision A. On reaching the 7th group we find the element Mn which while displaying the proper maximum positive valence of 7 is not nearly so strongly and typically electro-negative as the elements in division A of this group. Similarly the electro-positive element Cu of Group 1 on the opposite side of the loop, while displaying the proper positive valence for an element of this group, does not display it as strongly as do the elements of subdivision A of the same group. In other words, the transition from one side of the loop to the other is gradual, instead of abrupt, as on a primary loop. In accord with this behavior we find that in place of a transition element belonging to Group 0, with a valence of 0, we have the triad, Fe, Co, Ni, belonging to Group 8. The properties of this group are intermediate in character between those of the 7th and 1st groups on each side of it, thus completing the gradual character of the transition from back to front through this transition group.

This group is also characterized by a maximum positive valence of 8 and, according to Abegg, by a dormant negative valence of 0. We thus see that the transition from the back to the front of the cylinder on a secondary loop involves a change of valence from $(-1, +7)$, through $(-0, +8)$, to $(-7, +1)$, but on a primary loop the change is from $(-1, +7)$ through (0) to $(-7, +1)$. Moreover in the latter case the transition is through a peak occupied by a single inert element, while in the former it is around a smooth bend occupied by a series of three elements.

Stated in other terms the transition from the back to the front of the cylinder can occur only: (1) abruptly, through a group whose algebraic valence sum is 0 and whose arithmetical valence sum is also 0; or (2) gradually, through a group whose algebraic valence sum is 8 and whose arithmetical valence sum is also 8; while the transition from the front to the back of the cylinder can occur only through a group whose algebraic valence sum is 0 and whose arithmetical valence sum is 8.

Abegg himself, however, preferred[6] to assign the valence values +0 and −8 or −0 and +8 to the 0-group, the hypothetical value 8 being regarded as completely dormant. On this basis the arithmetical valence sum of all transition groups would evidently be 8. Abegg also preferred to regard Groups 0 and 8 as subdivisions A and B respectively of a single group, pointing out that as we proceed along the cylinder (Fig. 59) from right to left, on either the back or the front, the differences between the two subdivisions of a given group increase rapidly. Thus the difference between Ti and Ge or between Zr and Sn is small. The difference between P and V or between Sc and Ga, while somewhat greater, is still comparatively small. When we reach Groups 1 and 7, however, we find that K, Rb, and Cs on the one hand are quite decidedly different from Cu, Ag and Au on the other, and there is really little resemblance between Mn and Cl or Br. Abegg concludes, therefore, that in the next group this difference between the subdivisions should reach a maximum and accordingly considers Group 8 as the B-subdivision of Group 0. This viewpoint is indicated in Fig. 59 by connecting the two groups with a dotted tie-line. The tie-lines of the other groups can be made progressively heavier in the direction of Group 4 to indicate the convergence of the two subdivisions as Group 4 is approached.

The following variation in the statement of Abegg's rule has been suggested by Harkins:[7] If we define as *complementary* any two groups which face each other across the cylinder, then the group numbers (and hence also the maximum oxygen valences) of any two complementary groups when added together will always total 8. Thus starting with Group 4, which is to be considered as complementary to itself, we get 4+4, 3+5, 2+6, 1+7, and 0+8. Moreover, if with Abegg we may assign the value −8 as a valence number to Group 0, it is likewise true that if we add algebraically the most characteristic valence numbers of two complementary groups, the result will always be 0. Thus beginning with Group 4 again, we obtain 4−4, 3−3, 2−2, 1−1, and 8−8 or 0−0, the relationship being somewhat forced as regards the last pair.

Returning now to our journey around the cylinder, after completing the first secondary loop we return at Ge to the primary type and complete one full turn around the cylinder ending at Zr. Here we traverse again another secondary loop containing an undiscovered element in Group 7B. At Sn we return to the primary type and complete a full turn around the cylinder ending with Ce. Here a cataclysm of some kind appears to take place. Instead of making another loop around the cylinder, a return (see Fig. 59) to the Group-3A rod is made (or perhaps Ce itself belongs on this rod) and a vertical drop from atomic number 59 to atomic number 72 and from atomic weight 140 to atomic weight 174 takes place, fourteen elements of the rare earth group, one of which is yet to be discovered, occupying the interval. At all events the arrangement shown is correct if the relationships among these elements are those indicated. Our knowledge of these elements is still in an unsatisfactory state, however, and their proper distribution in the periodic system is therefore somewhat uncertain as indicated by the manner in which they are treated in Fig. 58 which makes no attempt to arrange them.

Whether a 4th-group element following lutecium exists at the place marked ? in Fig. 59 is doubtful, as Moseley's arrangement leaves no vacancy in the atomic numbers at this point. However this may be, the normal course of events is resumed once more with Ta and a full loop of the regular secondary type is completed ending with Pb and showing an undiscovered element in Group 7B. In the place occupied by Pb are also indicated (in Fig. 59) its numerous isotopes. After Pb comes a full turn of the primary type of loop occupied by the radio-elements and showing two vacancies, in Groups 7A and 1A respectively. The weak radioactivity displayed by potassium and rubidium lends color to the supposition that they may possibly contain traces of the missing radioactive element or group of isotopes belonging in the Group 1A vacancy. If such an element exists, it cannot belong to any of the known radioactive series, however (as is evident from Fig. 57), and its radioactive behavior might well be of a different type.

The primary loop containing the radio-elements ends at Io. Beginning here, another loop of the regular secondary type is started, but it goes no farther than U in Group 7B. If there are any elements of higher atomic weight, they have not yet been discovered.

It will be noticed that as the bottom of the cylinder is approached there appears to be a tendency for all of the elements (except those of Group 0) to become more metallic in character. On some helical models this convergence of properties is indicated by employing a truncated cone instead of a cylinder as a support for the helix.

Another peculiarity of the table, as pointed out by Harkins,[7] is the fact that the elements fall into periods as follows (see Fig. 59): Periods 1 and 2 contain 2×2^2 elements each, Periods 3 and 4 contain 2×3^2 elements each, Period 5 contains 2×4^2 elements, and Period 6 is incomplete. This peculiar relationship is doubtless connected with the genesis of the elements and if extrapolated upward on Fig. 59 would point to the possible existence of one or two elements with atomic weights lower than hydrogen. The existence of such elements in some of the stars and nebulæ has been inferred from certain lines in the spectra of these bodies. The names proto-hydrogen, nebulium, protofluorine, and arconium have been assigned to some of these hypothetical astronomical elements and an ingenious theory of their structure has been worked out by Nicholson[a] who has thus been able to predict the positions of many of the lines in their spectra, in some instances before these lines were actually observed in the stars.

A more detailed consideration of the properties of the elements and the periodic relations shown by them belongs more properly to the subject of Descriptive Inorganic Chemistry and will not therefore be further considered here.

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[a] J. W. Nicholson. Since 1912 Professor of Mathematics in Kings College at the University of London.

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APPENDIX

THERMODYNAMIC DERIVATIONS

The Perfect Thermodynamic Engine

1. Introduction.—In the preceding pages it has been frequently necessary to employ various purely thermodynamic equations, the derivations of which were not given. It was merely stated that they were necessary consequences of the First and Second Laws of Thermodynamics. It is the purpose of the present chapter to indicate the methods by which these important and fundamental relationships are derived. For this purpose we shall make use of a **perfect thermodynamic engine** (X, 8) arranged so that it can be driven by the physico-chemical reaction under consideration. The student who familiarizes himself with the use of this engine will find thermodynamic derivations greatly simplified and after a little practice will find that the desired result can usually be written down simply by inspection. Furthermore, the exact significance of each of the quantities involved in the result is made perfectly clear by the nature of the processes which accompany the operation of the engine.

2. Description of the Engine.—Figs. 60 and 61 illustrate types of the engine, the essential parts of which are the following (see Fig. 60):

Two *reaction chambers*, **E** and **E′** (the "boilers"), contain the system under consideration. Each chamber is placed in a *reservoir*, **R** and **R′**, of infinite heat capacity, for the purpose of maintaining a constant temperature within the chamber. Each chamber is fitted with a set of *cylinders*, **A, B, D, A′, B′, D′**, etc., which connect with it, when necessary, through suitable *semi-permeable membranes*, **aa, a′a′**. The cylinders are fitted with *frictionless* pistons, **A, B, D, A′, B′, D′**, etc., which may be semi-permeable or impermeable as required. Each corresponding pair of pistons is connected by a *rigid* piston rod, thus forming a *compound piston*, **AA′, BB′, DD′**, etc. The piston rods have zero heat capacities and are non-conductors of heat and electricity, and the two reservoirs, **R** and **R′**, are otherwise insulated from each other so that no irreversible transfer of heat can take place between them. By irreversible transfer of heat is meant a flow of heat from a higher to a lower temperature without the production of maximum work (X, 7 and 8).

3. The "Operation" of the Engine.—The "*operation*" of the engine consists in the movement of the compound pistons through finite distances, accompanied by corresponding processes which take place within the reaction chambers. These processes constitute the physico-chemical reaction under consideration and the process which takes place in chamber **E** must always be *exactly the reverse* of the process which occurs in chamber **E′**.

During the *operation* of the engine the following conditions must be fulfilled: (1) The two reservoirs must never differ from each other in temperature by more than an infinitesimal amount; when such a difference exists, the temperature of **R** will be designated by T and that of **R′** by $T+\mathrm{d}T$; (2) the pressure *difference* against the two heads of a compound piston must never exceed an infinitesimal amount; the pressures exerted against the pistons of **E** will be designated by p, P, Π, etc., those exerted against the pistons of **E′**, by $p+\mathrm{d}p$, $P+\mathrm{d}P$, $\Pi+\mathrm{d}\Pi$, etc.; (3) each compound piston must always move so as to produce the maximum amount of external work, there being applied to it a compensating external pressure substantially equal to the pressure difference on the two piston heads; and (4) the rates of motion of all the pistons must be so regulated that the equilibrium within the reaction chambers remains undisturbed. In other words, *the engine must always operate reversibly.*

4. The Work Performed by the Engine.—According to the Second Law the work, dA, performed by a perfect heat engine operating between the temperatures T and $T+\mathrm{d}T$ is (see X, 8 and 11)

$$\mathrm{d}A = Q\,\frac{\mathrm{d}T}{T} \tag{1}$$

where Q, the heat absorbed at the higher temperature, represents the heat effect (reckoned as heat *absorbed*) of the physico-chemical reaction which takes place in the chamber **E′**. Just what this reaction is in a given case will be perfectly clear by watching the operation of the engine. If $\mathrm{d}T=0$, that is, if the process is an isothermal one, then evidently $\mathrm{d}A=0$ also. After the operation of the engine the desired result is obtained simply by writing down the work performed by each of the compound pistons and placing the sum equal to $Q\frac{\mathrm{d}T}{T}$, or to zero, as the case may be.

In reckoning the work performed by any given compound piston it should be remembered that the piston always moves under an infinitesimal constant pressure difference and that hence the expression for the work which it performs will always be of the form $v\mathrm{d}p$, where v is the volume through which the piston moves. (Cf. equation 3, X.) In some instances $\mathrm{d}p$ may be zero.

It should also be noted that the algebraic expression for the work performed by any compound piston during the operation of the engine will have a *positive sign* when the motion is from *right to left* and a *negative sign* when the motion is from *left to right.* This convention with regard to the sign of the work is of course an arbitrary one. The reverse convention would do equally well.

5. The Method of Using the Engine.—The beginner will find it helpful to adopt a definite procedure to be employed in every instance. The following general procedure is recommended for this purpose. It is applicable to every case where it is desired to derive a differential equation which is a direct consequence of the Second Law of Thermodynamics alone. The procedure is conveniently divided into three stages which should be invariably followed in the order given.

I. Filling the Engine.—Fill *both* chambers of the engine with the physico-chemical system under consideration and designate the vapor and osmotic pistons which it is desired to employ. The pressures (p, Π, etc.) against these pistons will be the same on both sides of the engine. The lower piston **DD′** will be used as the *total-pressure piston* in every case, that is, the pressure exerted against it from each side represents the total external pressure P applied to the systems in the two chambers. Bring the heat reservoirs **R** and **R′** both to the temperature T. The engine is now filled but is not yet ready for operation because the pressures against the opposite heads of each compound piston are exactly equal in every case and there is no tendency for any piston to move. Clamp each piston and proceed to step *II.*

II. Changing the Variables.—On the right-hand side of the engine, increase the value of the independent variable by an infinitesimal amount. The independent variable in any case is the quantity whose effect upon the system we wish to ascertain. Then indicate the corresponding increase in each of the dependent variables, that is, in each of the quantities whose variation with respect to the independent variable we wish to discover. The changes in the dependent variables should always be indicated as *increases* without stopping to consider whether the change is really an increase or a decrease. This question will take care of itself. We are now ready for the operation of the engine.

III. Operating the Engine.—In the chamber **E′** allow the physico-chemical reaction under consideration to proceed to completion in the direction desired. *At the same time* move the necessary pistons reversibly in such directions as to maintain the physical condition and chemical composition of the system in chamber **E′** exactly what it was at the moment of beginning the operation. The reaction in chamber **E** will be found to proceed in the reverse direction and the condition of the system in this chamber will also remain at all times just what it was at the beginning of the operation. If the student is careful to see that this condition is fulfilled, it will be impossible for him to operate the engine incorrectly.

IV. Formulating the Result.—Write down the total work performed by the various pistons as directed in section 4 above and place the result equal to $Q\frac{dT}{T}$ or to zero, as the case may be.

In place of the letter Q, however, use a symbol indicating more specifically the nature of the heat effect of the process taking place in chamber **E′**. Finally rearrange the equation so that the left-hand side is a partial differential coefficient, indicating as subscripts the quantities or variables which are constant for the process under consideration.

The use of the above method of procedure will be more clearly understood by considering some specific examples. The cases considered in what follows include the derivations of most of the thermodynamic equations employed in this book. In the first few cases considered the method of procedure outlined above will be gone through in detail, but afterward it will be sufficient to indicate the condition of the engine just before beginning the operation; that is, the first two steps of the method of procedure will be left for the student to carry out.

VAPOR PRESSURE

6. The Vapor Pressure of a Pure Substance. (*a*) **Statement of the Problem.**—The equilibrium between vapor and liquid (or vapor and crystal) in a one-component system may be altered: (*a*) by changing the total pressure on the liquid (or crystal) phase at constant temperature; (*b*) by changing the temperature of the system while keeping the pressure on the liquid (or crystal) phase constant; or (*c*) by changing the temperature of the system and at the same time allowing the total pressure on the liquid (or crystal) phase to vary in such a manner that it is always equal to the vapor pressure. We shall make use of the perfect thermodynamic engine in order to determine the separate effects of these different factors upon the vapor pressure of a pure liquid. The treatment for the case of a pure crystal is *perfectly analogous*, as is also the final equation obtained.

(*b*) **The Pressure Coefficient** ($T=$**const.**).—We shall use the engine shown in Fig. 60, *omitting*, however, pistons and cylinders **BB′**.

I. The engine is filled as follows: Chamber **E** is filled with the liquid whose vapor pressure, acting through the membrane **aa** (permeable to the vapor only) against piston **A**, is p. The total pressure on the liquid, acting against piston **D**, is P. Temperature of $\mathbf{R}=T$. Chamber **E′** is filled exactly as **E**.

II. Change the pressure on piston **D′** from P to $P+\mathrm{d}P$. The pressure on piston **A′** will then become $p+\mathrm{d}p$, and the engine is ready for operation.

III. Piston **AA′** moves reversibly from right to left (under the pressure difference, $\mathrm{d}p$), while one mole of the liquid in chamber **E′** vaporizes through membrane **a′a′** into cylinder **A′** and one mole[1] of

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[1] Strictly, the amounts of material which are vaporized and condensed respectively during the motion of the compound piston **AA′** are not exactly equal but differ from each other by an infinitesimal amount. This difference need not be considered, however, as the amount of work involved in equalizing it would be a differential of the second order and therefore negligible. (See Jour. Amer. Chem. Soc., **32**, 472–474 (1910).)

the vapor in cylinder **A** condenses through membrane **aa** into chamber **E**. At the same time piston **DD′** moves reversibly from left to right (under the pressure difference, dP), through the volume, V_0, of one mole of the liquid. The work done by piston **AA′** is v_0dp, where v_0 is the volume of one mole of the vapor at the temperature T and pressure p. The work done by piston **DD′** is $-V_0dP$. We have, therefore,

$$v_0dp - V_0dP = 0 \tag{2}$$

or

$$\left(\frac{\partial p}{\partial P}\right)_T = \frac{V_0}{v_0} \tag{3}$$

which is equation (7, XII).

If the vapor obeys the perfect gas laws, equation (2) assumes the form

$$\left(\frac{\partial \log_e p}{\partial P}\right)_T = \frac{V'_0(1-\beta P)}{RT} \tag{4}$$

where V'_0 is the molal volume of the liquid under zero pressure and β is the mean coefficient of compressibility of the liquid as defined by the equation, $\beta = \frac{(V'_0 - V)}{V'_0P}$. The equation can now be integrated. Since the right-hand member of equation (3) is necessarily positive, the vapor pressure always increases with increase in pressure on the liquid phase. The coefficient, $\left(\frac{\partial p}{\partial P}\right)_T$, is small for temperatures considerably removed from the critical temperature (thus for water at 0°, $\left(\frac{\partial p}{\partial P}\right)_{T=273°} = 3.6 \cdot 10^{-6}$ mm. per atmosphere) but increases with the temperature and becomes equal to 1 at the critical temperature.

(*c*) **The Temperature Coefficient** (*P* = **const.**).—Let us now consider the effect of temperature changes upon the vapor pressure of a liquid which is under constant external pressure P, such changes as would occur, for example, on heating the liquid in an open vessel exposed to the atmospheric pressure. As in the previous case, we will make use of the engine shown in Fig. 60, omitting cylinder **BB′**.

I. The engine is filled as follows: Chamber **E** is filled with the liquid, whose vapor pressure, acting through the semipermeable (*i.e.*, only to the vapor) membrane against piston **A,** is p. Total pressure on liquid, acting against piston **D,** is P. Temperature of $\mathbf{R} = T$. Chamber **E′** is filled exactly as **E.**

II. Change the temperature of reservoir **R′** from T to $T + \mathrm{d}T$. The pressure against piston **A′** will then become $p + \mathrm{d}p$. The pressure against piston **D′** remains P, however, by the conditions of our problem. The engine is now ready to operate.

III. Piston **AA′** moves reversibly from right to left (under the pressure difference, $\mathrm{d}p$), while one mole of the liquid in chamber **E′** evaporates through the membrane **a′a′** into cylinder **A′** and one mole[1] of the vapor in cylinder **A** condenses through membrane **aa** into chamber **E.** At the same time piston **DD′** moves from left to right (under the pressure difference, zero) through the volume, V_0, of one mole of the liquid. This is necessary in order that the pressure upon the liquid in both chambers shall remain constant.

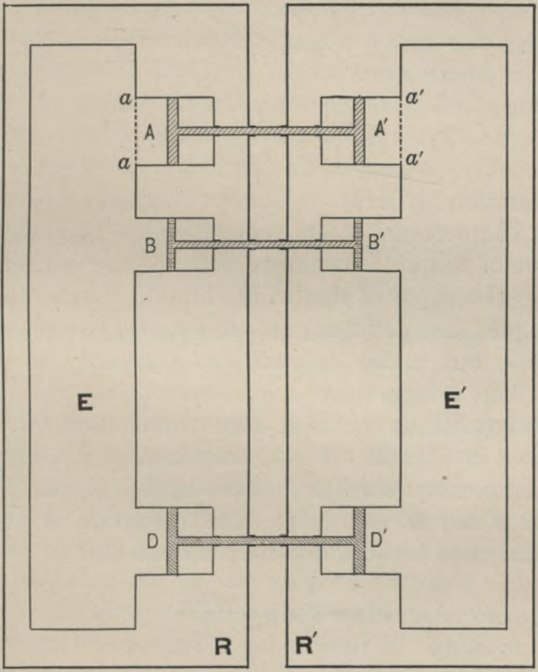

FIG. 60.

IV. The work done by piston **AA′** is $v_0\mathrm{d}p$, where v_0 is the molal volume of the vapor at the temperature T and pressure p. The work done by piston **DD′** is zero because the pressures are the same on both sides of it. The heat absorbed from reservoir **R′** is the molal heat of vaporization L_v of the liquid at the temperature T and the constant pressure P, because vaporization of the liquid under these conditions is the physico-chemical reaction which takes place in chamber **E′** during the operation of the engine. We have, therefore,

$$v_0\mathrm{d}p = L_v\frac{\mathrm{d}T}{T} \tag{5a}$$

or

$$\left(\frac{\partial p}{\partial T}\right)_P = \frac{L_v}{v_0 T} \tag{5b}$$

which is equation (1, XII).

(*d*) **The Temperature Coefficient** ($P=p$).—The latent heat of vaporization of a liquid is usually determined by condensing (in a calorimeter) the vapor of the boiling liquid. Under these conditions the liquid always forms, not under constant pressure at all temperatures, but under its own vapor pressure at each temperature. The temperature coefficient of the vapor pressure under these conditions can be at once written down, by using the engine shown in Fig. 60. The arrangement is exactly as in the preceding case *except that the pressure against piston* **D** *is* p *and that against piston* **D′** *is* $p+\mathrm{d}p$. The operation is exactly the same as before and we obtain at once the relation

$$v_0\mathrm{d}p - V_0\mathrm{d}p = \frac{L_v\mathrm{d}T}{T} \tag{6a}$$

or

$$\left(\frac{\partial p}{\partial T}\right)_{P=p} = \frac{L_v}{(v_0 - V_0)T} \tag{6b}$$

which is the Clausius-Clapeyron equation, equation (2, XII).

Problem 1.—Carry out the above derivations using a crystalline substance instead of a liquid.

Problem 2.—Derive, with the aid of the engine, an expression for the coefficient $\left(\frac{\partial T_F}{\partial P}\right)$, the rate of change of the freezing point with the external pressure: (1) when the pressure on both phases is the same; and (2) when the pressure on the crystalline phase, only, is varied.

7. The Vapor Pressures of the Constituents of a Solution.—If we are dealing with the partial vapor pressure of one of the constituents of a solution instead of with the vapor pressure of a pure liquid, the derivations are carried out exactly as above except that the chambers of the engine are made infinite in volume. This is necessary in order that the removal or insertion of one of the constituents, as a result of the motion of the vapor piston **AA′**, shall not produce a change in the composition of the solution. The final equations obtained will be identical in form with those given above except that for V_0 we will write $\overline{V}_0$, the partial molal volume (XII, 3) of the constituent in the solution, and for L_v we will write $\overline{L}_v$, the partial molal heat of vaporization of the constituent from the solution. The exact significance of these partial quantities will be clearly evident from the operation of the engine.

Problem 3.—Derive equation (8, XII). (See Jour. Amer. Chem. Soc., **32**, 477–481.)

THE THERMODYNAMIC RELATIONS CONNECTING THE COLLIGATIVE PROPERTIES OF A SOLUTION

8. Description of the Engine.—The type of engine used is shown in Fig. 60. Both chambers are filled with the solution under investigation. Piston **AA′** is a "*vapor piston*," that is, as it moves reversibly toward the left, for example, it draws the vapor of the solvent out of chamber **E′** and condenses it into chamber **E**. Piston **BB′** is an "osmotic piston." As it moves reversibly toward the left it allows solvent to enter chamber **E′** by passing through the semipermeable head **B′**, while at the same time solvent is removed in a similar manner from chamber **E**, the space behind the two piston heads being filled with pure solvent. Piston **DD′** is the total-pressure piston. It moves to the right or left during the operation of the engine whenever a volume change in the chambers renders it necessary, but since in the following treatment we shall deal always with a solution under constant external pressure (that of the atmosphere, for example), this piston will move only under a pressure difference of zero. Consequently no work is involved in its motion and it will not be necessary to pay any attention to it during the operation of the engine.

For our solution we shall take any homogeneous liquid mixture of any number of constituents, A, B, C, etc. Since the terms solvent and solute are perfectly arbitrary for such a solution (XI, 4), any constituent of the solution may be considered as the solvent in the following derivations.

9. Osmotic Pressure and Vapor Pressure (P, $T =$ **const.**).—To ask the question, "How does the vapor pressure of the solvent from any solution vary with the osmotic pressure?," is equivalent to asking the question, "How does the vapor pressure of the pure liquid solvent vary with the total pressure upon it?" (see definition of osmotic pressure, equation (12, XII)), and this relation has already been derived. It is equation (3), which may be written as follows (since by definition $d\Pi = -dP$):

$$\left(\frac{\partial p}{\partial \Pi}\right)_{P,T} = -\frac{V_0}{v_0} \tag{7}$$

This is equation (15, XII). See problem 1, XII, for its integration.

Problem 4.—Derive equation (7) directly by means of the engine.

10. Osmotic Pressure and Freezing-point Lowering ($P =$ **const.**).—The problem may be stated thus: "How does the osmotic pressure of a solution change with the temperature at which the solution is in equilibrium with the pure crystalline solvent?" The arrangement of the engine, ready for operation, is as follows:

Chamber **E**: Filled with a solution in equilibrium with an excess of pure crystalline solvent and therefore (XI, 8) at the temperature of its freezing point, T_F. The mole fraction of the solvent is x. The pure liquid solvent (in cylinder **B**) is in equilibrium with the solution through the osmotic membrane of the piston head, the pressure difference on the two sides of the membrane being Π.

Chamber **E′**: Exactly as chamber **E** except that the mole fraction of the solvent is $x + dx$, the freezing point $T_F + dT_F$ and the osmotic pressure $\Pi + d\Pi$.

$d\Pi$ in this instance is given by the expression

$$d\Pi = \left(\frac{\partial \Pi}{\partial T}\right)_x \left(\frac{\partial T_F}{\partial x}\right)_P dx + \left(\frac{\partial \Pi}{\partial x}\right)_T dx \tag{8}$$

To operate the engine allow one mole of crystalline solvent to melt in chamber **E′** and remove the resulting liquid osmotically with piston **BB′** which moves reversibly toward the right. The reverse operation occurs in chamber **E**. The work done by piston **BB′** is $-V_0 d\Pi$. The heat absorbed at the higher temperature (*i.e.*, from reservoir **R′**) is the molal heat of fusion (L_F) of the crystalline solvent, under the pressure P, to form liquid solvent under the pressure $P-\Pi$, when this process takes place reversibly. This heat of fusion differs from the ordinary one merely by the value of the heat of compression of the liquid from P to $P-\Pi$. This difference is negligible for most practical purposes.

We have, therefore,

$$-V_0 d\Pi = \frac{L_F dT_F}{T_F} \tag{9}$$

or

$$\left(\frac{\partial \Pi}{\partial T_F}\right) = -\frac{L_F}{V_0 T_F} \tag{10}$$

which is equation (17, XII). For the integration of this equation see Jour. Amer. Chem. Soc., **32,** 498 and 1636 (1910).

11. Vapor Pressure and Freezing Point (*P* = **const.**).—The problem may be stated as follows: "How does the vapor pressure of the solvent from a solution vary with the temperature at which the solution is in equilibrium with the pure crystalline solvent?" Now the vapor pressures from the solution and the crystalline solvent are equal when the two are in equilibrium (X, 10); consequently this question is the same as inquiring, "How does the vapor pressure of the pure crystalline solvent vary with the temperature?," and this relation has already been derived. It is equation (5) which we may write as follows (using T_F in place of T to indicate that we mean the absolute temperature of the freezing point of the solution):

$$\left(\frac{\partial p}{\partial T_F}\right)_P = \frac{L_S}{v_0 T_F} \tag{11}$$

which is equation (14, XII).

In this equation L_S is the molal heat of sublimation of the pure crystalline solvent under the pressure P to form saturated vapor at the pressure p. dp is expressed by the equation

$$dp = \left(\frac{\partial p}{\partial T}\right)_x \left(\frac{\partial T_F}{\partial x}\right)_P dx + \left(\frac{\partial p}{\partial x}\right)_P dx \tag{12}$$

Problem 5.—Derive equation (11) directly by means of the engine. Integrate the equation for water, on the assumption that the specific heat capacities of ice and its saturated vapor are equal. (Cf. equation (21, XX).)

CHEMICAL EQUILIBRIUM

12. Statement of the Problem.—Let us consider any chemical equilibrium, expressed by the equation

$$aA+bB+\ldots.\rightleftarrows mM+nN+\ldots. \qquad (13)$$

in which a mols of the substance A react with b mols of the substance B, etc., to form m mols of the substance M and n mols of the substance N, etc. The substances entering into the reaction are in equilibrium with each other in any homogeneous phase and there may or may not also be present in the phase one or more other substances which do not take part in the reaction, a solvent or an indifferent gas, for example. The composition of the phase is represented by the equation

$$x_A+x_B+\ldots.+x_M+x_N+\ldots.+x_1+x_2+\ldots.=1 \qquad (14)$$

where x_A is the mole fraction of the constituent A, etc., numerical subscripts referring to substances which do not take part in the chemical equilibrium.

Our problem is to determine in what direction and to what extent the chemical equilibrium is displaced by: (1) increasing the concentration (*i.e.*, the mole fraction) of one of the reacting substances; (2) increasing the total pressure on the phase; and (3) increasing the temperature of the system. In deriving our fundamental equations it will be simpler to fix our attention chiefly upon some particular phase, and we shall choose a gaseous phase which, in addition to the reacting substances, contains also an indifferent gas which we shall call constituent 1. It would correspond to a solvent, if we were dealing with a liquid solution.

13. Arrangement of the Engine.—We shall make use of the engine shown in Fig. 61. The arrangement when ready for operation is as follows:

Chamber **E**: Filled with the gaseous mixture as described above, the composition of the mixture being represented by the equation

$$x_A+x_B+\ldots+x_M+x_N+\ldots.+x_1=1$$

The substances A, B,.. M, N,.. are in chemical equilibrium as expressed by the equation

$$a\mathrm{A}+b\mathrm{B}+\ldots\rightleftarrows m\mathrm{M}+n\mathrm{N}+\ldots.$$

The partial pressures of the substances taking part in the equilibrium act through suitable semipermeable membranes against the pistons as follows: p_{A} against piston **A,** p_{B} against piston **B,** p_{M} against piston **M,** and p_{N} against piston **N.** The total pressure on the system as applied by piston **D** is P.

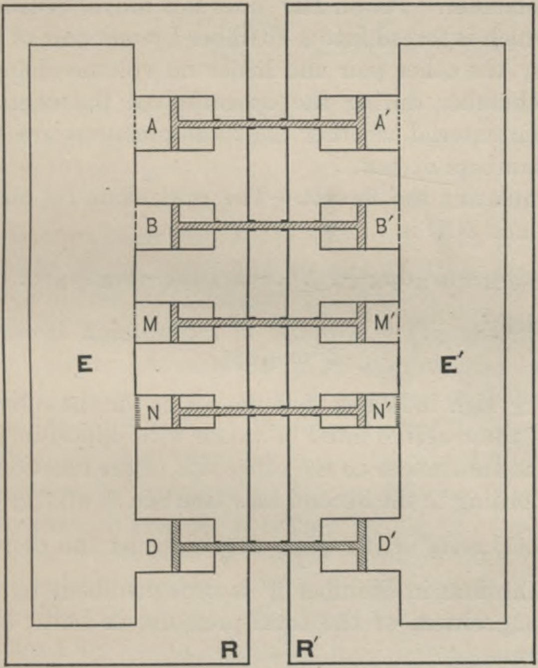

FIG. 61.

Chamber **E′:** Analogous in every respect to chamber **E** except that the equilibrium has been slightly displaced by some cause so that the partial pressures from this chamber have become $p_{\mathrm{A}}+\mathrm{d}p_{\mathrm{A}}$ against piston **A′,** $p_{\mathrm{B}}+\mathrm{d}p_{\mathrm{B}}$ against piston **B′,** etc.

14. Operation of the Engine.—The operation of the engine consists in the movement of pistons **AA′** and **BB′** toward the right until a moles of A and b moles of B have been forced into **E′** and drawn out of **E**; and the simultaneous movement of pistons **MM′** and **NN′** toward the left, removing m moles of M and n moles of N from **E′** (as fast as they are formed by the reacting of the A and B which are being introduced by pistons **AA′** and **BB′**) and forcing them into **E** (as fast as they are required to replace, by reaction, the A and B which are being removed by pistons **AA′** and **BB′**). The equilibrium is thus not disturbed in either chamber. Piston **DD′** does not move, because all the material which is forced into a chamber by one pair of pistons is removed by the other pair and hence no volume change occurs in either chamber during the operation of the engine. It is therefore immaterial whether the total pressures are the same in both chambers or not.

15. Formulating the Result.—The work done by pistons **AA′**, **BB′**, **MM′** and **NN′** is

$$mv_{\mathrm{M}}\mathrm{d}p_{\mathrm{M}}+nv_{\mathrm{N}}\mathrm{d}p_{\mathrm{N}}+\ .\ \ .\ \ .-av_{\mathrm{A}}\mathrm{d}p_{\mathrm{A}}-bv_{\mathrm{B}}\mathrm{d}p_{\mathrm{B}}-\ .\ \ .\ \ .$$

or more briefly,

$$\Sigma^{\pm}mv_{\mathrm{M}}\mathrm{d}p_{\mathrm{M}}$$

where the ± sign indicates that the terms for the substances on one side of the reaction must be taken with opposite signs from those for the substances on the other side of the reaction.

Now according to the Second Law (see Sec. 4, above) this work is equal to (1) zero, or (2) $Q\frac{\mathrm{d}T}{T}$, according as the displacement of the equilibrium in chamber **E′** is brought about by changing (1) the composition, or the total pressure, or both; or (2) the temperature.

In the former case we have, therefore,

$$\Sigma^{\pm}mv_{\mathrm{M}}\mathrm{d}p_{\mathrm{M}}=0 \qquad (15)$$

which is equation (4, XXII). In this equation dp *for each substance* represents the complete differential, $\mathrm{d}p=\left(\frac{\partial p}{\partial P}\right)_x\mathrm{d}P+\left(\frac{\partial p}{\partial x}\right)_P\mathrm{d}x$, P being the total pressure on the system and x the mole fraction of *any constituent* of the system whether it be concerned in the chemical reaction or not. In other words, if the chemical equilibrium be displaced in one direction or the other by changing either the pressure or the composition of the gas or both, the corresponding changes in the partial pressures of the molecular species concerned in the equilibrium must occur in such a way as to fulfill the condition represented by equation (15).

If the shift in the equilibrium is brought about by changing the temperature of chamber **E′** from T to $T+\mathrm{d}T$, we obtain equation (43, XXII) which is

$$\left(\frac{\Sigma \pm m v_{\mathrm{M}} \partial p_{\mathrm{M}}}{\partial T}\right)_P = \frac{H_P}{T} \tag{16}$$

where H_P, the heat-of-the-reaction (XIX, 5), is the heat *evolved* when the reaction as written takes place at *constant pressure, from right to left*, that is, so as to produce the substances A and B.

In the operation of the engine it will be noted that in chamber **E′** the reaction proceeds from *left to right*, that is, so as to produce M and N, and hence, according to section 4 above, H_P is the heat *absorbed* during this process.

16. Chemical Equilibrium in Solution.—The thermodynamic laws governing chemical equilibrium in solution may be conveniently derived in terms of the osmotic pressures of the substances concerned in the equilibrium. The operation of the engine is very similar to that described above for gases, the chief difference being that the substances involved in the equilibrium are removed from and introduced into the chambers by means of osmotic pistons instead of vapor pistons. Thus if the chambers contain a dilute solution of the substances A, B, M, and N in chemical equilibrium with one another, then cylinder **A** will be separated from chamber **E** by means of a membrane permeable only to the substance A and containing (in front of the piston) a dilute solution of A at such a concentration, C_{A}, that it is in osmotic equilibrium with the solution in chamber **E.** The piston **A** is an osmotic piston permeable only to the pure solvent and only the pure solvent is contained in that portion of the cylinder behind the piston head. Piston and cylinder **A′** are similarly arranged.

Now then if piston **AA′** be moved reversibly toward the right, the solvent will flow through the semipermeable head of piston **A** and will thus dilute the solution of A contained in the cylinder. This solution will then no longer be in osmotic equilibrium with the solution in chamber **E** and in order to restore the equilibrium the substance A will pass through the membrane **aa** from chamber **E** into cylinder **A**. The reverse operation occurs on the other side of the engine and we thus see that the motion of the osmotic piston **AA′** from left to right results in the removal of A from chamber **E** and the introduction of A into chamber **E′**, just as in the case of a vapor piston moving in the same direction. The other three pistons are arranged similarly and if, for example, reservoir **R** is at the temperature T and reservoir **R′** at the temperature $T+\mathrm{d}T$, the operation of the engine gives us

$$\Sigma^{\pm} mv_{\mathrm{M}}\mathrm{d}\Pi_{\mathrm{M}} = Q\frac{\mathrm{d}T}{T} \tag{17}$$

where Q is the heat *absorbed* when the reaction, $a\mathrm{A}+b\mathrm{B}=m\mathrm{M}+n\mathrm{N}$, takes place in dilute solution under such conditions that it performs the maximum amount of external work, for this is what happens in reservoir **R′** during the operation of the engine.

Now the work performed by chamber **E′** during the operation is (neglecting differential quantities)

$$W_{max} = mV_{\mathrm{M}}\Pi_{\mathrm{M}} + nV_{\mathrm{N}}\Pi_{\mathrm{N}} - aV_{\mathrm{A}}\Pi_{\mathrm{A}} - bV_{\mathrm{B}}\Pi_{\mathrm{B}} \tag{18}$$

and for a dilute solution, according to equation (28, XIV), $\Pi V = RT$ for each mole of solute, thus giving us

$$W_{max} = (m+n-a-b)RT \tag{19}$$

According to the First Law of Thermodynamics we have

$$\Delta U = Q - W \tag{20}$$

and hence

$$Q = \Delta U + (m+n-a-b)RT \tag{21}$$

Now by definition

$$V = \frac{1}{C}$$

and from equation (28, XIV) we obtain

$$\Pi = CRT \tag{22}$$

and by differentiation

$$\mathrm{d}\Pi = RT\mathrm{d}C + RC\mathrm{d}T \tag{23}$$

and

$$V\mathrm{d}\Pi = RT\mathrm{d}\log_e C + R\mathrm{d}T \tag{24}$$

Combining this with equation (17) above gives

$$\Sigma^{\pm}(RT\mathrm{d}\log_e C_{\mathrm{M}}^m + mR\,\mathrm{d}T) = Q\frac{\mathrm{d}T}{T} \tag{25}$$

which on combination with equation (21) becomes

$$(m+n-a-b)R\mathrm{d}T + RT\mathrm{d}\log_e \frac{C_{\mathrm{M}}^m \cdot C_{\mathrm{N}}^n}{C_{\mathrm{A}}^a \cdot C_{\mathrm{B}}^b} = [\Delta U + (m+n-a-b)RT]\frac{\mathrm{d}T}{T} \tag{26}$$

or

$$\frac{\mathrm{d}\log_e K_c}{\mathrm{d}T} = \frac{\Delta U}{RT^2} \tag{27}$$

which is equation (49, XXII).

HEAT CAPACITY

17. The Difference between c_p and c_v.—Equation (1, XX) is a consequence of the First and Second Laws together and is derived as follows:

For 1 gram of any substance we obtain from equation (29, XX) differentiating with respect to T, at constant pressure,

$$\left(\frac{\partial Q}{\partial T}\right)_p = c_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p \tag{28}$$

Equation (30, XX) gives us (for $m=1$)

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v \tag{29}$$

whence

$$c_p - c_v = \left(\frac{\partial U}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v + p\left(\frac{\partial v}{\partial T}\right)_p \tag{30}$$

Moreover, since $U = \mathrm{f}(v,T)$, if p is constant, the differential calculus requires that

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_v \tag{31}$$

which on combining with equation (30) gives

$$c_p - c_v = \left[\left(\frac{\partial U}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p \tag{32}$$

Thus far we have made use of the First Law only.

According to the Second Law, for any process involving a volume change, Δv, under a constant pressure, p, we have the relation

$$\mathrm{d}A = v\mathrm{d}p = Q\frac{\mathrm{d}T}{T} \tag{33}$$

or

$$Q = T\frac{v\mathrm{d}p}{\mathrm{d}T} \tag{34}$$

If the volume change is an infinitesimal one, the heat absorbed will also be infinitesimal and equation (34) may be written

$$\mathrm{d}Q = T\frac{\mathrm{d}v\mathrm{d}p}{\mathrm{d}T} \tag{35}$$

or

$$\left(\frac{\partial Q}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v \tag{36}$$

From equation (29, XX), differentiating with respect to v at constant T, we find

$$\left(\frac{\partial Q}{\partial v}\right)_T = \left(\frac{\partial U}{\partial v}\right)_T + p \tag{37}$$

whence by combination with equations (32) and (36) we have

$$c_p - c_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p \tag{38}$$

which is equation (1*a*, XX).

Problem 6.—Remembering that for any substance $v = \mathrm{f}(p, T)$, show how equation (1*a*, XX) may be transformed into (1*b*, XX). This transformation is purely mathematical.

MISCELLANEOUS PROBLEMS FOR ADVANCED STUDENTS

The student is supposed to find whatever additional data are required for the solution of the following problems and to exercise his judgment in the selection of the best values to employ for the case in hand. In some instances essential data may not be available in the literature. In such cases the student should use the knowledge which he has acquired of the laws and principles of his science in order to estimate as accurately as possible the required values. The Landolt-Börnstein-Meyerhoffer *Physikalische Chemische Tabellen* and the *Annual Tables of Physical and Chemical Constants* will give most of the data required. Give the source of all data employed and justify all assumptions made.

Problem 1.—The following data concerning an elementary substance in the gaseous state are known: (*a*) Combined with a basic element it gives a strong base-forming compound and with an acid element, a strong acid-forming compound; (*b*) its molal heat capacity at constant pressure is 6.96 cal.; (*c*) its sulphur compound has a vapor density, referred to hydrogen, of 32 and contains 50 per cent. of sulphur; (*d*) 1 gram of the elementary substance in the gaseous state at 0° and 760 mm. occupies a volume of 700 c.c. What conclusions concerning the atomic and molecular weights of the elementary substance can be drawn from each datum alone and from all the data together? State the principle involved in each conclusion.

Problem 2.—(*a*) The compound of a certain element with silver contains 46.0 per cent. of silver. (*b*) 10 grams of this (solid insoluble) compound at 80° introduced into 800 grams of water at 20° cause its temperature to rise 0.046°. (*c*) The compound is isomorphous with silver chloride. (*d*) The elementary substance itself has in the gaseous state a specific volume of 200 c.c. at 327° and a pressure of one atmosphere. (*e*) At higher temperatures the specific volume increases much more rapidly than proportionality to the absolute temperature would require. (*f*) The specific-heat-ratio of the vapor is 1.31. State just what conclusion in regard to the atomic weight of the element and its mol. wt. in the gaseous state is warranted by (*a*) alone; by (*a*) and (*b*); by (*a*) and (*c*); by (*a*) and (*d*); by (*a*), (*d*), and (*e*); and by (*a*), (*d*), and (*f*). State the principle involved in each conclusion.

Problem 3.—What conclusion concerning the atomic weight of an element can be drawn from each of the following data: (1) separately; (2) from (*a*) and (*d*) together; (3) from (*a*) and (*e*) together; (4) from all the data together? (*a*) 0.4481 gram of the element yielded an oxide weighing 0.6024 gram. (*b*) Two chlorides are known, one with a vapor density (referred to air) of 6.14 and the other with a vapor density (referred to air) of 4.86. (*d*) With ammonium sulphate the element forms a double sulphate which is isomorphous with ammonium chrome-alum. (*e*) The specific heat capacity of the solid oxide is 0.1062 calorie per degree. (*f*) An aqueous solution of the chloride has a strong acid reaction. State the principle involved in each conclusion.

Problem 4.—Estimate (to within one- or two-tenths of a degree) the boiling point, under atmospheric pressure, of a solution of 8.91 grams of phenanthrene in 100 grams of 2–3-dimethylhexane. (See Jour. Amer. Chem. Soc., **33,** 521 (1911).)

Problem 5.—The ionization constant of NH_4OH in aqueous solution at 18° is $17.2 \cdot 10^{-6}$. One liter of a 0.049435 normal aqueous solution of ammonia was shaken with 1 liter of chloroform until equilibrium was established. The chloroform layer on analysis was found to contain 0.001705 formula weight of NH_3. If 0.0207067 formula weight of ammonia is added to a bottle containing 1 liter of water and 1 liter of chloroform, how much will be present in each solvent when equilibrium is established at 18°? Ammonia exists as NH_3 molecules only, in chloroform. In water it is chiefly present as NH_3 molecules, but a small quantity hydrates to form NH_4OH which ionizes into NH_4^+ and OH^--ions.

(NOTE: Found by experiment, 0.0007067 equivalent in the water layer and 0.0200 equivalent in the $CHCl_3$ layer.)

Problem 6.—To a solution of two isomeric substances, A and B, in equilibrium with each other, a third substance, C, is added which does not react with A but reacts slowly and finally completely with B according to the reaction $B + C = D$. The equilibrium between A and B establishes itself instantaneously. Derive an equation which will express the concentration [D] of the substance D after a time *t*, in terms of the original concentrations [A], [B], and [C], and the velocity constant *k* of the slow reaction.

Problem 7.—Diazoacetic ester decomposes in aqueous solution according to the equation, $CHN_2 \cdot CO_2C_2H_5 + H_2O = CH_2OH \cdot CO_2C_2H_5 + N_2$, and the reaction is catalyzed by hydrogen-ion. At 25° in a solution 0.1 normal in acetic acid, 37.5 per cent. of the ester is decomposed in 10 minutes. Assuming that it takes 67 minutes to decompose the same percentage of the ester in a solution 0.1 formal in sodium hydrogen tartrate, what is the hydrogen-ion concentration in that solution? How many c.c. of N_2 (measured under standard conditions) will be evolved in half an hour at 25° from 1 liter of a 0.25 molal solution of the ester to which is added 0.1 mole of butyric acid and 0.05 mole of sodium butyrate?

Problem 8.—A dilute solution of sodium chloride is flowed through a cylindrical tube with platinum gauze electrodes 25 cm. apart, in such a direction and at such a rate that the migration toward the anode of the hydroxide ions formed at the cathode is just compensated, a constant difference of potential of 50 volts being maintained at the electrodes.

Calculate the rate expressed in cm. per hour at which the solution is flowing through the tube. Assume that the degree of ionization of the sodium hydroxide in the presence of the sodium chloride is 85 per cent.

Problem 9.—At $T_0°$ the degree of dissociation of the substance A_aB_b in the gaseous state according to the reaction $2A_aB_b = aA_2 + bB_2$ is α_0, the total pressure being P_0. If V_1 liters of A_aB_b at the temperature T_0 and pressure P_1 are mixed with V_2 liters of B_2 at the temperature T_2 and pressure P_2, and the temperature of the mixture is maintained at T_0 and its pressure at P_3, what will be the degree of dissociation (α_3) of A_aB_b in this mixture?

Problem 10.—When hydriodic acid is heated to 440° until equilibrium is reached it is 25 per cent. dissociated into H_2 and I_2. A mixture of 5.67 grams of solid iodine and 1 liter (measured under standard conditions) of hydrogen is heated to 440°, the volume being kept at 1 liter. All the iodine vaporizes. (*a*) What per cent. of it will be combined with the hydrogen? (*b*) What will be the total pressure of the mixture and its density referred to hydrogen? (*c*) If the total pressure on the system be decreased 50 per cent., how much iodine will be combined under the new pressure?

Problem 11.—The equilibrium constant of the reaction, $N_2 + O_2 = 2NO$ at 2675° absolute is $\dfrac{[NO]^2}{[N_2]\,[O_2]} = K_c = 3.5 \cdot 10^{-3}$. What yield of NO (in per-cent. by volume) would one obtain at this temperature and at atmospheric pressure (1) from air, (2) from a mixture of 40 per cent. O_2 and 60 per cent. N_2? What should be the initial composition of the gaseous mixture in order to give the maximum yield of NO?

Problem 12.—In each of two bottles are placed 1 liter of water and 50 c.c. of a saturated solution of picric acid in benzene. 0.03 mole of HCl is added to the first bottle and 0.025 mole of another acid (X) to the second bottle, both of these acids being insoluble in benzene. The two bottles are then rotated at 18° until equilibrium is established, after which the benzene layer is drawn off from each bottle and analyzed. The analyses show the same content of picric acid in the benzene layers in both bottles. Calculate the hydrogen-ion concentration in a 0.025 molal aqueous solution of the acid X.

Problem 13.—Calculate the heat of neutralization of RbOH by HBr in dilute solution at 100°. (See Table XXVIII.)

Problem 14.—Calculate the hydrogen-ion concentration of a solution obtained by dissolving 61.55 liters (measured dry at 27° and 76 cm.) of NH_3 gas in 2.5 liters of a 0.01*n* aqueous solution of NH_4Cl at 18°.

Problem 15.—The acid HA has at 18° an ionization constant of $3.4 \cdot 10^{-8}$ and the Λ_0 value of the anion is 180. What will be the conductance of a 0.01 normal solution of the sodium salt of this acid at 18°, between parallel circular electrodes 2 cm. in diameter and 7 cm. apart in a tube of 2 cm. internal diameter? (?, Hydrolysis.)

Problem 16.—(*a*) The ionization constant of *l*-mandelic acid is $4.17 \cdot 10^{-4}$ and that of acetic acid $1.8 \cdot 10^{-5}$. From these data calculate, approximately, the ratio in which the base NaOH will distribute itself between the two acids, if 0.5 equivalent of the base be added to a liter of solution containing

0.5 equivalent of each acid. (*b*) The mixture of base and acids mentioned above was placed in a 10-decimeter tube and its angular rotation measured by means of a polariscope and found to be −18.07°. In the same tube a 0.5 normal solution of Na-*l*-mandelate gave −17.07° and a 0.5 normal solution of *l*-mandelic acid gave −22.70°. If, however, one-fourth of an equivalent of HCl was added to a liter of the mandelic acid solution, the rotation was increased to −22.92°. From these data compute another value for the distribution ratio asked for under (*a*).

Problem 17.—At 18° the specific conductance of a 0.1250 formal solution of the weak acid diketotetrahydrothiazole (C_3NH_3OS) is $47.1 \cdot 10^{-6}$ reciprocal ohms. The equivalent conductance of the anion of this acid is the same as that of the acetate ion. 50 c.c. of an approximately 0.2 normal solution of this acid are to be titrated with 0.2*n* KOH *at* 18°. What is the value of the "indicator function" of the indicator best adapted for use in this titration. Assuming the indicator to be half transformed at the end point, which of the indicators shown in Table XXIX would be the best one to employ?

Problem 18.—In the analysis of ground waters a commonly occurring case is a water which contains carbonic acid in excess of the amount required to form *bicarbonate* with the base present. Assume that this excess carbonic acid ("free carbonic acid") amounts to about 0.0003 mole of CO_2 per liter (an "acidity of 30 parts per million") and the total carbonate (*i.e.*, CO_2 as acid or normal carbonate) to about 0.007 mole of CO_2 per liter (an "alkalinity of 700 parts per million"). The total-ion concentration of the water is about 0.01 equivalent per liter. The "free" CO_2 is to be determined by titration with 0.01 normal NaOH and the "combined" CO_2 by titration with 0.01 normal HCl. Calculate the best value of the indicator function for each of these titrations.

Problem 19.—200 grams of mercury vapor at a temperature of 250° are allowed to expand adiabatically from an initial volume of 123.0 liters to a final volume of 500.0 liters, the pressure at the same time falling to 23.203 mm. Assuming the perfect gas laws, calculate the specific heat capacity of the vapor (*a*) at constant pressure and (*b*) at constant volume.

Problem 20.—Calculate thermodynamically the atomic heat capacity, at constant volume, of solid iodine at room temperatures.

Problem 21.—Determine the change in total energy which occurs when one mole of orthonitrobenzoic acid changes from the ionized state to the crystalline state at 20°, using the following experimental data: (1) 500 grams of a $\frac{1}{2}$ wt. normal solution of KOH were first saturated with the orthonitrobenzoic acid at 19° and this solution was removed from the excess solid and placed, together with a piece of thin gold foil, in an adiabatic calorimeter at 19.20°. 573 grams of a $\frac{1}{2}$ wt. normal solution of HNO_3 at 19.20° were then run in and after stirring, the temperature rose to a constant maximum value of 20.00±0.01°. (2) The precipitate in the calorimeter was collected, dried and enclosed in the piece of gold foil so as to form a flat compact capsule. This was placed in the clean calorimeter together with 500 grams of the KOH solution and the whole brought to 17.00°. 573

grams of the HNO_3 solution at the same temperature were then run in and a maximum temperature of 20.05° attained. The heat of neutralization of KOH by HNO_3 ($\frac{1}{2}n$) at 20° is 13,720 cal. per mole. The solubility of orthonitrobenzoic acid in water at 20° is 0.0379 mole and the degree of ionization of the saturated solution, as obtained from conductance measurements, is 33.6 per cent. The laws of mass action and of solubility product may be assumed to hold for the orthonitrobenzoic acid in all of the above solutions. What improvements in experimental details would you suggest?

Problem 22.—The heat (H_P) evolved by the reaction $4Ag+O_2=2Ag_2O+H_P$, is 13,400 cal. at 25° and constant pressure. Derive thermodynamically an equation expressing the change in H_P with the temperature, $\left(i.e., \frac{\mathrm{d}H_P}{\mathrm{d}T}\right)$. Using the best numerical data that you can find calculate the heat of this reaction at 200°. Assume that oxygen is a perfect gas.

Problem 23.—A mixture of hydrogen and oxygen in equivalent proportions at 20° and 760 mm. is exploded in a closed bomb placed in a calorimeter whose initial temperature is 20°. After the explosion it is found that for each gram of hydrogen in the bomb 342 grams of ice must be added to the calorimeter in order to restore its temperature to 20°. The heat of fusion of ice at 0° may be taken as 79.6 cal. Assuming (1) that at the end of the experiment all of the water produced by the explosion is in the liquid form, (2) that the explosion inside the bomb is so rapid that no heat is lost to the walls of the bomb until the reaction is complete, and (3) that the reaction goes to completion at all temperatures, what would be the maximum temperature and pressure attained inside of the bomb. The molal heat of vaporization of water at 100° and constant volume is 9000 cal. and the molal heat capacity of water vapor is $C_v=8.6+0.0038t$. Assume the perfect gas laws.

Problem 24.—A certain substance occurs in two modifications, A and B, the melting points of which are both higher than the transition point. At 38° C. both forms exist, but A is the more stable form at this temperature. Which has the lower melting point, A or B? Prove it.

Problem 25.—The vapor pressure of ethyl ether at 40° is 900 mm. By what percentage (approximately) will this vapor pressure change if the total pressure on the liquid is increased by three atmospheres?

Problem 26.—With the aid of the perfect thermodynamic engine derive an expression for the rate of change of transition temperature with external pressure. The transition temperature of rhombic into monoclinic sulphur is 95.5° when the pressure is one atmosphere. How much and in what direction will the transition temperature be changed per atmosphere increase in pressure? Use Reicher's value for the heat of transition. The difference between the specific volumes, v_m and v_r, of monoclinic and rhombic sulphur at the transition point was determined by means of a dilatometer and found to be $v_m-v_r=0.0126$ c.c. (Reicher found experimentally that the transition temperature changed 0.04°—0.05° for each atmosphere increase in pressure.)

Problem 27.—Calculate thermodynamically the vapor pressure of ice at the temperature of boiling air (80° abs.). What would be the relative humidity at 25° of air which had been dried by passing it through a coil immersed in liquid air?

Problem 28.—In the purification of H_2 gas the last traces of O_2 are removed by passing the gas through a layer of platinized asbestos or spongy platinum at a temperature of 300° C. What will be the partial pressure of O_2 in H_2 prepared by this method if the procedure is as follows: The gas is passed slowly over a long layer of the spongy platinum at 300° and then after cooling to 0° is passed through a glass spiral immersed in liquid air. This process is repeated several times. For additional data see problem 27 above and problem 40, XXII.

Problem 29.—The vapor pressure of nitrobenzene, $C_6H_5NO_2$, at 99.3° is 20 mm. When a mixture of the mutually insoluble liquids, water and nitrobenzene, is heated under a pressure of one atmosphere it boils at 99.3°. What mass of distillate must be collected in order to obtain a yield of 100 grams of nitrobenzene?

Problem 30.—A solution of dibromsuccinic acid is boiled with water. The initial concentration of the dibromsuccinic acid is 5.11 units per liter. At the end of the first ten minutes it has fallen to 3.77 and at the end of the next ten minutes to 2.74 units per liter. From these data calculate two values of the specific reaction rate. Take the average of these results and compute the concentration of the dibromsuccinic acid at the end of one hour. (The actually measured concentration at the end of an hour was 0.80 unit.) (Cf. XXI, 2.)

Problem 31.—At 18° the solubility product for AgCl is $1.11 \cdot 10^{-10}$. If conductivity water having a specific conductance of $0.4 \cdot 10^{-6}$ mhos at 18° is saturated with AgCl at this temperature, what will be the specific conductance of the saturated solution?

Problem 32.—To one liter of a solution containing 0.1 mole of cane sugar a mixture of 0.1 mole of KCl and 0.01 mole of HCl is added and the initial rate of inversion found to be R moles of sugar per second. What will be the initial rate of inversion of a 0.13 molal cane sugar solution produced by adding to one liter of it, 0.1 mole of the nitrate of a weak base, the nitrate being 7 per cent. hydrolysed in the solution.

Problem 33.—Two substances, A and B, have the same melting point (50°), but do not form mixed crystals. They form a compound (consisting of $33\frac{1}{3}$ mole per cent. of A) which melts at 25°. Draw a figure which will represent the freezing-point-solubility diagram for this system.

Problem 34.—State the number of degrees of freedom possessed by each of the following systems: (1) ice, crystals of NaCl, soln. of NaCl in H_2O; (2) crystals of benzene, ice, soln. of H_2O in benzene, soln. of benzene in H_2O; (3) crystals of benzene, crystals of NaCl, ice, aqueous solution, vapor; (4) crystals of alcohol, ice; (5) ice, soln. of alcohol in water; (6) crystals of SO_2-hydrate, ice, soln. of water in liquid SO_2, soln. of SO_2 in water, vapor.

Problem 35.—Mr. A claims to have found an exception to the Second Law of thermodynamics, based upon the following data: He prepared in a high state of purity a new and very stable crystalline substance. Three very careful determinations of the melting point by the capillary tube method gave 103.22°, 103.21° and 103.23°, respectively. The vapor pressure of the crystals was determined at 99°, 100°, 101°, 102° and 103°, using the differential tensimeter, in a thermostat regulated to 0.01°, the tensimeter being kept a week at each temperature previous to making the reading. The vapor pressure of the liquid was then determined at 103.25°, 104°, 105° and 106° without opening the apparatus. Both sets of measurements were then repeated in the reverse direction. On plotting the data the two series on the crystals and the two on the liquid checked very closely. The two vapor pressure curves, however, intersected at 101.13°. The same thermometer was used throughout the work and all corrections to it were properly made. The substance did not form a second crystal phase but melted *sharply* to a clear liquid. The heat of fusion was about 40 cal. per gram and the change in volume on melting (determined by melting under oil) was 0.1 cc. per gram. State whether you agree or disagree with Mr. A's claim and defend your opinion. (Cf. X, 10 and Prob. 2, Appendix.)

SUBJECT INDEX

AUTHOR INDEX

Biographical sketches are indicated by black face type

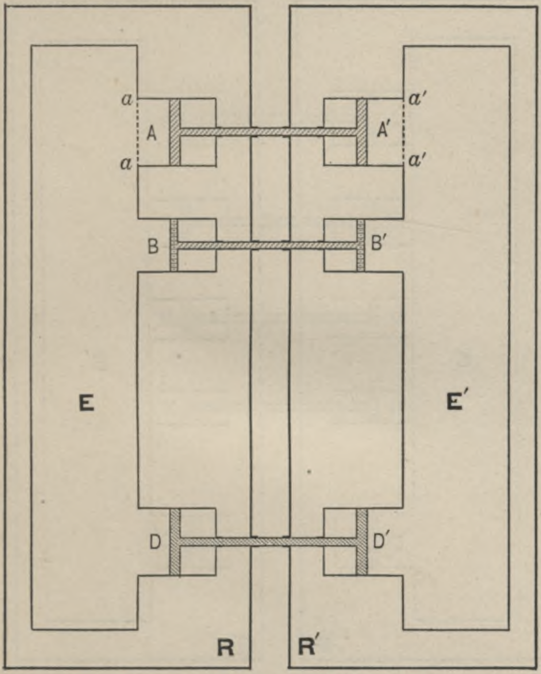

Fig. 60.

Note.—Since Figs. 60 and 61 will need to be referred to frequently, it was deemed advisable to print them on a separate, perforated sheet, which is bound at the back of the book, so that it can be torn out for ready reference.

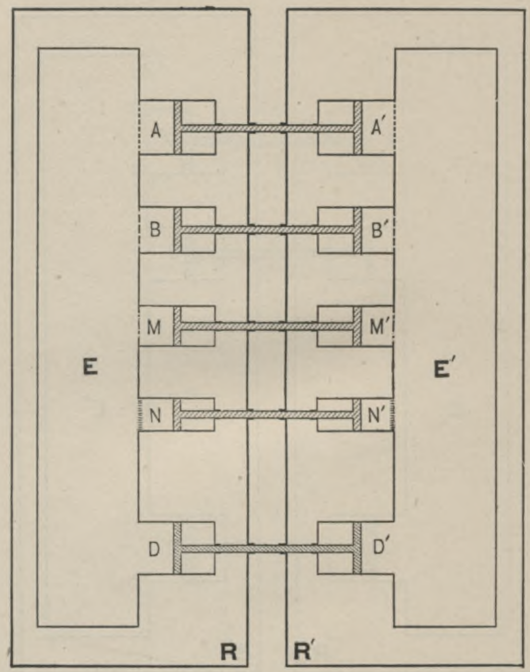

Fig. 61.